THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE POLYMERIZATION OF RING-SUBSTITUTED STYRENES AND THE DEGRADATION OF THEIR POLYMERS

by

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PREFACE

The work described in this thesis was carried out in the Chemistry Department of the University of Glasgow.

I would like to thank Professor J.M.Robertson for the privilege given to me to work in this department.

I wish to express my gratitude to Dr.N.Grassie who suggested the topic of research and supervised the work, for his encouragment and guidance and for granting me a research scholarship for over a year. Iwould also like to thank him for his personal kindness and consideration.

I would also like to thank Dr.I.C.McNeill for the use of the degradation apparatus and the osmometer.

My thanks are also due to the general technical assistance provided by Messrs R.Smith, G.Perrit and I.Orr and to the glass blowing and engineering workshops of the Chemistry Department.

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A.A.A.M.Rizkallah.

LIST OF CONTENTS

Page No.

CHAPTER 1

INTRODUCTION

A. General Comments[1,2]

In the last thirty years or so, the rapid advance of chemical knowledge together with a corresponding increase in the technological skills, has led to the commercial development of a large number of synthetic polymers which are now the basis of new materials in the manufacture of resins, fibres, textiles, paints, rubber and plastics.

Throughout the history of chemistry, chemical problems have been approached by synthetic and degradative routes. Both routes have contributed to our understanding of the structure and properties of these substances.

Interest in polymer degradation reactions was originally concerned with the elucidation of the molecular structure of naturally occuring polymers such as silk, wool, starch, cellulose, proteins and rubber.

In recent years however, since the commercial introduction and development of synthetic high polymers it has been necessary to investigate degradation for the better understanding of the behaviour and particularly the undesirable deterioration of physical properties of

commercial materials which occur under certain of the influences to which they are subjected in use, such as heat, light and oxygen.

From a fundamental point of view, initial progress in this problem has been slow, because it has often been necessary to await fuller investigation of polymerization mechanisms, so that the detailed structure of the polymers under consideration might be fully appreciated.

Hence, the degradation studies of high polymers both natural and synthetic, are of great technological interest, not only from the point of view of prevention of deterioration, but also in planning stable macromolecules and in the elucidation of polymer structure.

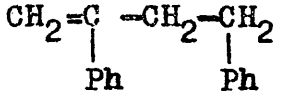
B. Early Experiments:

Because of the early application of polystyrene as a commercial polymer, and because its products of degradation are relatively simple, a great deal of the early polymer degradation work was focussed on this material, and it was known as early as 1866[3] to break down on heating to give high yields of monomer.

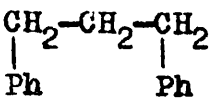
Because the chemical nature of the glassy solid polystyrene was not clearly understood; no detailed chemical study of its pyrolysis was carried out until the late twenties and early thirties when Staudinger and Steinhofer[4] were able to isolate the following compounds in addition to monomeric styrene:-

The Dimer Fraction:

2,4-Diphenyl-1-Butene.

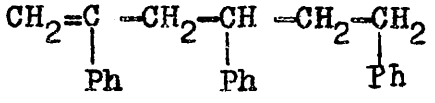


1,3-Diphenyl Propane.

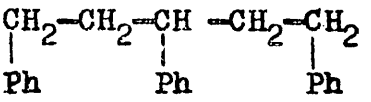


The Trimer Fraction:

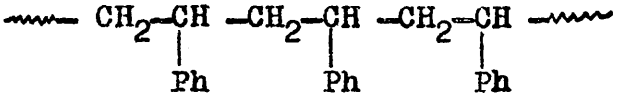
2,4,6-Triphenyl-1-Hexene.



1,3,5-Triphenyl Pentane.



Since none of the compounds isolated contained benzene rings on adjacent carbon atoms, they concluded that polystyrene itself, must consist of chains of styrene units in a head to tail sequence. This head to tail



structure, was disputed by Mack[5] and by Midgley, Henne and Leicester[6], but it has withstood all criticisms and is now generally accepted.

C. The Random Theory of Degradation:

The random theory of degradation of polymers emerged from the work of Meyer, Hopff and Mark.[7] Kuhn[8] and Freudenberg[9] applied the theory about 1930 to the hydrolytic degradation of starch and cellulose. During the hydrolysis of these compounds, the viscosity of the system decreases continuously, but appreciable amounts of the unit molecule, glucose, do not appear early in the reaction, although it is the ultimate product. These

results suggested a chain reaction occuring at random along the macromolecule.

The random theory of degradation was developed mathematically by Kuhn, whose statistical treatment, after slight modification[10,11] gave satisfactory agreement with experimental results.

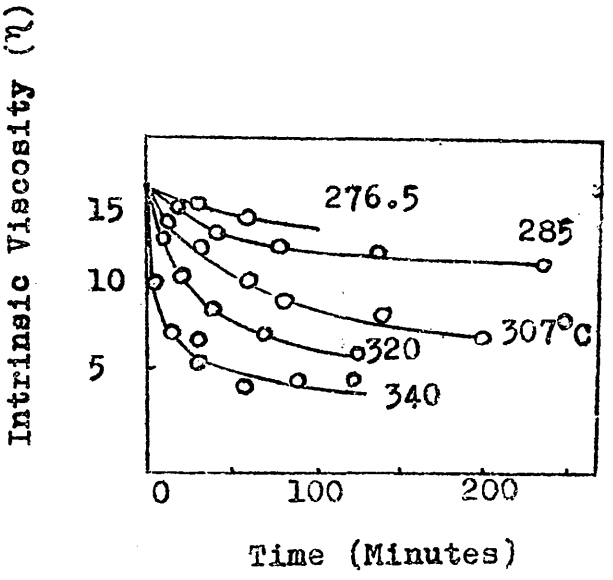
Since the degradation of synthetic polymers is accompanied by the production of the unit molecule or monomer, it was therefore natural to suggest the possibility of also applying the random theory to these compounds.

Staudinger and Steinhofer also gave a picture of the mechanism of degradation in terms of random scission, and later Votinov, Kobeko and Marei[12] who studied the thermal degradation of both polystyrene and polymethyl methacrylate, supported the random theory and claimed good agreement between experiment and Kuhn's mathematical treatment.

D. Rejection of the Random Theory of Degradation - The Introduction of the Weak Link Theory:

Later, more detailed experimental work by Jellinek[13,14] illustrated that the random scission theory had a number of serious shortcomings when applied to the thermal degradation of polystyrene. In particular, the molecular weight of the polymer falls rapidly to a limiting value, as shown in Fig.1, instead of continuously decreasing to very small values as required by the random

Figure 1.

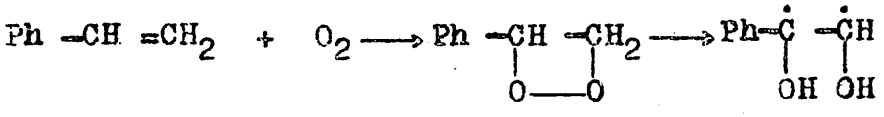


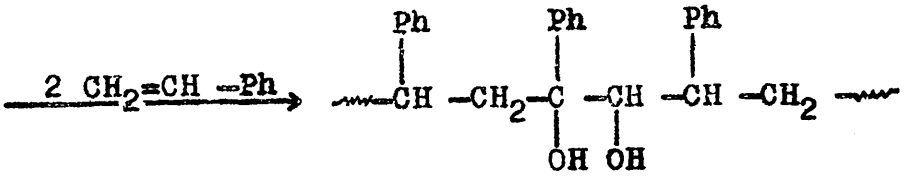
Decrease of Intrinsic Viscosity of Polystyrene with Time at Various Temperatures (Jellinek)

theory of degradation. Moreover, the rapid fall in molecular weight was accompanied by the production of monomer in quantities which were about 10^3 to 10^4 times larger than would be expected on the basis of a random mechanism. It was therefore becoming obvious that the random theory of degradation was not satisfactory for polystyrene.

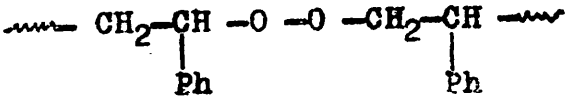
Jellinek concluded that the experimental results were best accounted for by postulating the existence of a limited number of weak links, distributed at random along the polymer chains, and that degradation ceases when all these weak links are broken.

Since it was well known at that time that traces of oxygen have a pronounced catalytic influence upon the course of the polymerization of styrene, Jellinek suggested that the weak links might be formed by incorporation of oxygen into the polymer chain during polymerization. This could occur either by hydroperoxidation





Or by direct copolymerization to give the structure:-



In order to account for the various features of the degradation reaction, Jellinek proposed that degradation is initiated by scissions at these weak links to produce radicals which subsequently split off monomer units. This accounts for the relatively large amounts of monomer produced early in the reaction.

The possibility that free radicals play a significant role in these degradation reactions was not clearly established till Grassie and Melville[15] re-examined the thermal degradation of polymethyl methacrylate at about the same time as Jellinek was studying polystyrene.

Grassie and Melville were able to show that this is a chain reaction which is initiated by the formation of radicals at the chain ends, which then split off monomer units in a reverse polymerization process. THey thus concluded that the degradation of polymethyl methacrylate is not a random process, as would have been revealed to Votinov et al, had they measured the molecular weights of their polymers during degradation.

The free radical nature of the polystyrene degradation reaction was later demonstrated by Jellinek and Spencer[16].

E. <u>The Role of Transfer in the Degradation of Polystyrene</u>:

Although traces of a variety of gaseous and liquid products are obtained when polystyrene is thermally

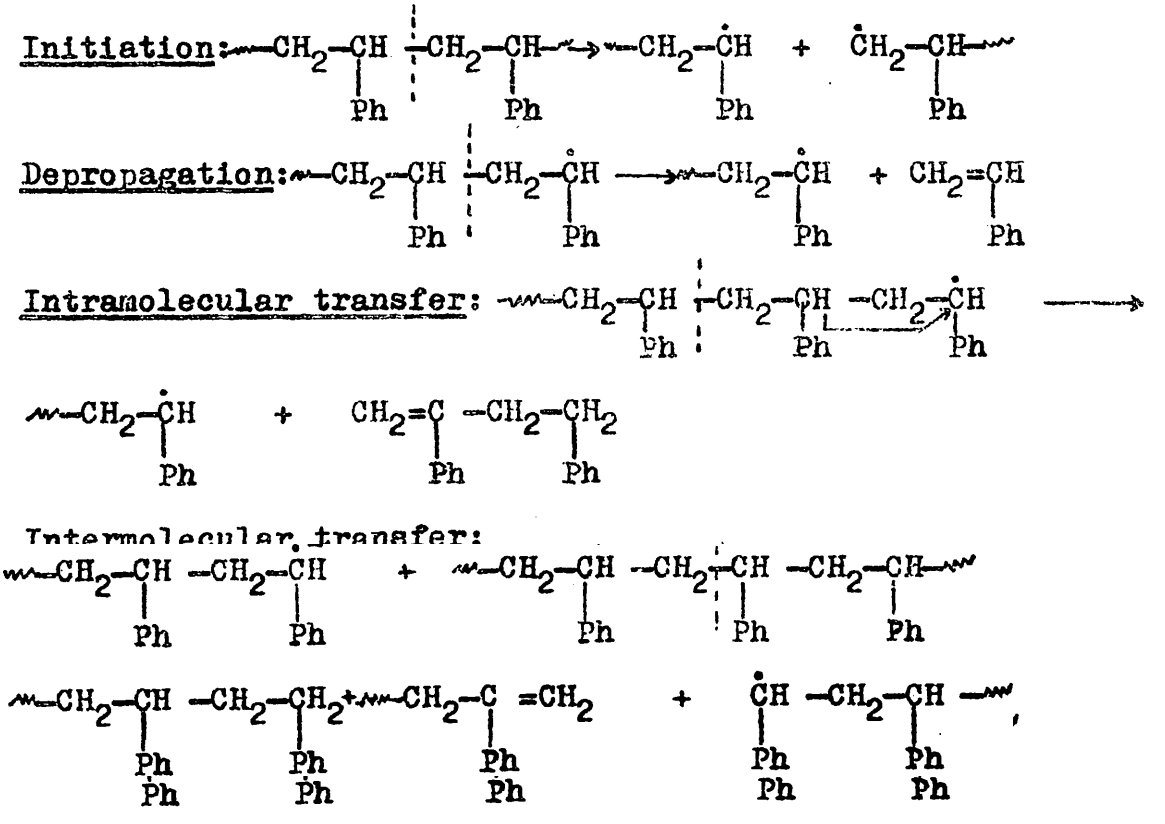
degraded,[17,18,19,20,21]. the principal products are styrene monomer and a wax like fraction,non volatile at room temperature,but volatile at the temperature of the reaction.This latter consists of a mixture of dimer, trimer,tetramer and pentamer.An involatile residue remains in the reaction vessel.

The presence of chain fragments such as dimer, trimer.....etc,suggests that chain transfer may play a significant part in the reaction.These products,together with the steep initial fall in molecular weight and a maximum in the rate curve,are the principal features of the reaction which must be explained.

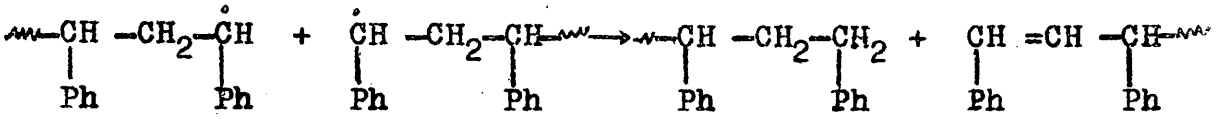
Simha and Wall[22,23] interpreted the reaction on the basis of a radical chain process,and derived a theoretical expression for the rate of conversion of a polymer to volatile material.They considered that initiation could occur at the chain ends or at random along the polymer molecule by a simple splitting of C— C bonds,followed by depropagation which produces monomer molecules.Depropagation may be in competition with intermolecular transfer or with intramolecular transfer.Intermolecular transfer is presumed to involve abstraction of a hydrogen atom from another molecule, leading to chain scission.In intramolecular transfer,a radical can react with a hydrogen atom from its own chain, which is assisted by local chain coiling,from the third

to the seventh carbon atom and may produce dimer, trimer. . . . .etc.

They suggested that at least two factors are important for transfer, namely; the reactivity of the radicals and the presence of susceptible hydrogen atoms along the polymer chain. Hydrogen atoms attached to substituted carbons, such as the reactive tertiary hydrogen atoms in polystyrene, are additionally activated by virtue of being attached to carbon atoms in the (α) position with respect to the phenyl residue. The mechanism may be represented as follows:-



Termination:



The characteristic feature of the theoretical expression of Simha and Wall is that it exhibits a rate maximum at 25% conversion. They explained the shift in maximum to (30-40)% conversions in Madorsky's[24] results to be due to the fact that quite large fragments may be able to evaporate at the reaction temperature.

Later, Madorsky and Straus[25] demonstrated the importance of the chain transfer reaction and showed the effect of molecular structure of chains and side groups on the rate, nature and amounts of volatile products obtained in the degradation of a variety of vinyl polymers. The percentages of monomer produced during degradation of several substituted polystyrenes are given in Table 1.

According to Simha and Wall's reaction mechanism higher chain fragments such as dimer, trimer.....etc., are produced by inter-and intramolecular transfer, involving the (α) hydrogen atom. Intramolecular transfer when it occurs at a point further along the chain, will produce the same effect as intermolecular transfer, resulting in chain scissions into involatile fragments and hence in a large decrease in the molecular weight of the polymer. Since monomer is produced by the depropagation

Table 1

Degradation as a Function of Molecular Structure

Polymer	Structure	Wt.% of Mono.
Polystyrene.	~~CH_2–CH(Ph)~~	42
Poly -β-deutero styrene.	~~CH(D)–CH(Ph)~~	42
Poly -M-methyl styrene.	~~CH_2–CH(Ph (CH_3))~~	44
Poly -γ-deutero styrene.	~~CH_2–C(D)(Ph)~~	70
Poly -α-methyl styrene.	~~CH_2–C(CH_3)(Ph)~~	100

step,the yield of monomer obtained during the degradation reaction will give some measure of the relative importance of the depropagation and transfer steps.

Thus in poly-α-methyl styrene the yield of monomer is 100%,indicating that transfer plays no part in the reaction.In polystyrene itself,however,the monomer yield is 42%.On substitution of methyl group for hydrogen in the benzene ring in poly-M-methyl styrene,the monomer yield is 44%,indicating that substitution in the ring has less effect than when the substitution is made in the (α) position on the back bone of the chain,and that transfer takes place at the tertiary hydrogen atom.This is further confirmed by the results of poly-α-deutero-styrene and poly -β-deutero styrene.In poly-α-deutero-styrene,the monomer yield is intermediate between ordinary polystyrene and poly-α-methyl styrene,as transfer involving a deuterium atom will require a higher energy of activation than that involving a hydrogen atom,When the deuterium atom is on the (β) carbon atom the yield of monomer is almost the same as that for ordinary polystyrene,as transfer of the (α) hydrogen atom takes place.

The above resulte are evidence that a transfer process of some kind is important in the thermal degradation of polystyrene,but it does not indicate whether the process is inter- or intramolecular transfer.

Accordingly, Brown, Hart and Wall[26] studied the pyrolysis of poly-α- and poly-β-deutero styrene. They compared the rates of degradation of these polymers with that of normal polystyrene. They assumed that if the initial fall in molecular weight is due to weak link scissions alone, as suggested by Jellinek, then the rate of degradation of poly-α-deutero styrene and that of ordinary polystyrene should be the same. If however, intermolecular trahsfer plays a significant part in the reaction, the rate of degradation of poly-α-deutero styrene should be less than that of normal polystyrene.

The rate of degradation as reflected by measurements of molecular weights of the residual material of the polymer as it degraded, was found to be about half that of normal polystyrene. They attributed this to an isotope effect during intermolecular transfer and concluded that in polystyrene the intermolecular transfer process is mainly responsible for the initial rapid fall in molecular weight of the polymer during degradation and not the weak link scissions.

In a later communication, Grassie[27] claimed that this evidence may be used, however, in support of weak link scission, since the presence of deuterium atoms could affect the rate of thermal break of the weak links.

This was the position when Grassie and Kerr started work. They agreed with Simha et al that the process was a radical depolymerization, but what was causing the sharp fall in molecular weight?

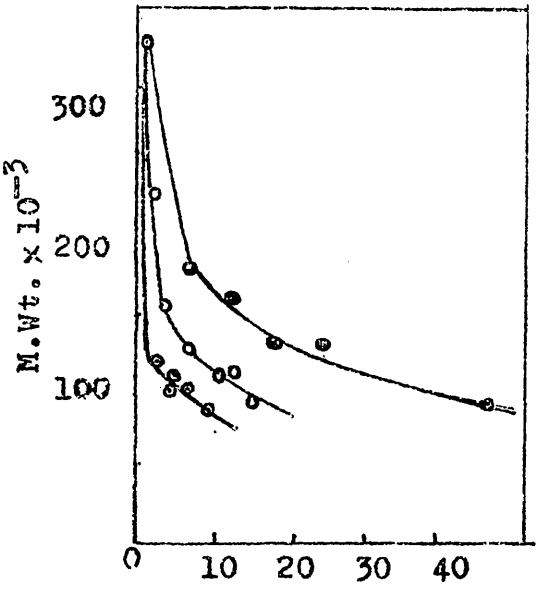
a) Weak links b) Transfer

F. The Work of Grassie and Kerr:

Grassie and Kerr showed first of all that the presence of oxygen[28] during the polymerization of styrene monomer is not the sole cause of weak links in the polymer, since these are still found in samples prepared from carefully purified monomer polymerized in vacuum.

Since weak links cannot be fully accounted for in terms of the effect of oxygen, they assumed that any labile structural abnormalities must be produced during the polymerization process, and that their concentration might be expected to depend upon some polymerization variables. This led them to the study of the effect on the concentration of weak links of a number of these variables, such as molecular weight, degree of conversion, initiator and temperature of polymerization. They found that the proportion of weak links depends only on the temperature of polymerization.[29] Moreover, the limiting value to which the molecular weight falls due to weak link scissions is independent of the degradation temperature as shown in Figs. 2 and 3 .

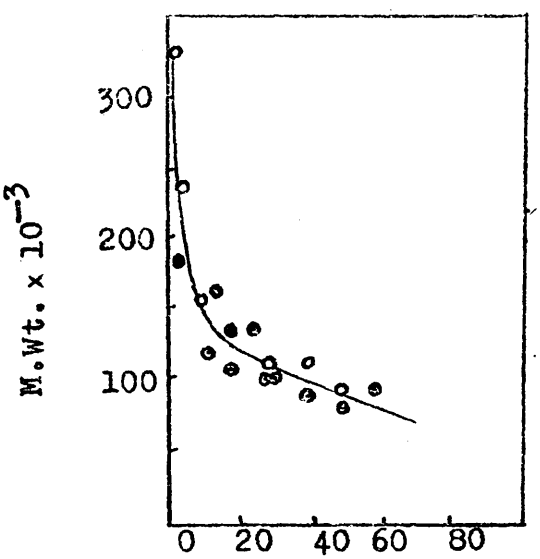
Figure 2



Molecular Weight Changes With Time In Polymer S_5

At 280°C, • ; 290°C, ○; 298°C, ◉ .

Figure 3

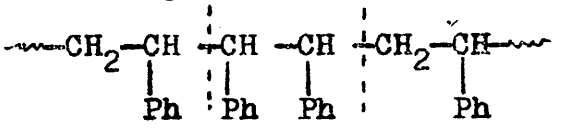


Molecular Weight Changes With Extent Of Volatilization In Polymer S_5 At 280°C,•; 290°C,○; 298°C,●.

G.The Work of Grassie and Cameron:

Grassie and Cameron studied the effect of head to head addition[30] on the course of weak link scissions in polystyrene degradation.They also studied the effect of solvents[27] and investigated the nature of weak links by ozonization[31].

They concluded from their results that head to head structures are not thermo-labile points in polystyrene This was deduced by means of styrene-stilbene copolymer degradation studies.The presence of stilbene units in



Styrene-Stilbene Copolymer.

polystyrene chains does not affect the degradation properties, as the limiting values of the molecular weights of the copolymers after degradation are not significantly lower than that of pure polystyrene prepared under the same conditions.

Moreover,they found that the rapid decrease in molecular weight which occurs in the initial stages of the degradation reaction,occurs at the same rate and to the same extent whether the reaction is carried out in bulk polymer or in naphthalene or tetralin solution.

On the other hand,evolution of volatile products from the radical chain depropagation process initiated

at the chain ends,which occurs in bulk polymer and in naphthalene solution,is completely inhibited in tetralin solution.In other words,the rate of evolution of volatile material is affected by the medium,while the rate of weak link scissions in all are identical,which is a further indication that volatilization and molecular weight decrease are two distinct processes.(see Fig.4)

Those authors also studied the change of molecular weight of polystyrene on ozonolysis and found that the initial decrease in the molecular weight is the same as that which occurs during thermal weak link scissions. In addition,the molecular weight of polystyrene in which weak links have been destroyed thermally does not decrease on ozonization.

They interpreted their results by assuming that weak links in polystyrene are associated with unsaturation in the main polymer chains,resulting from the formation of quinonoid type structures during polymerization,by reaction of polystyryl radical in one of the resonance forms in which the radical center exists in the benzene ring:-

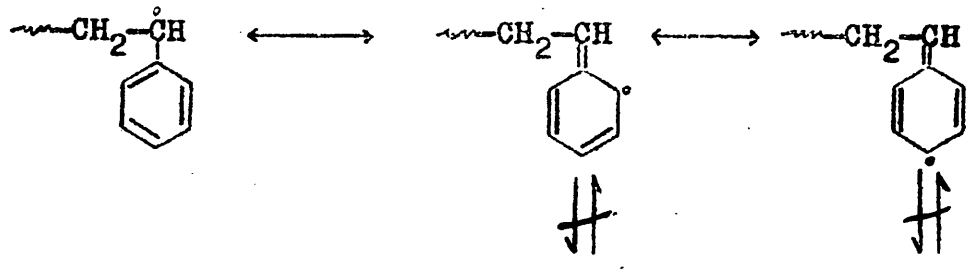
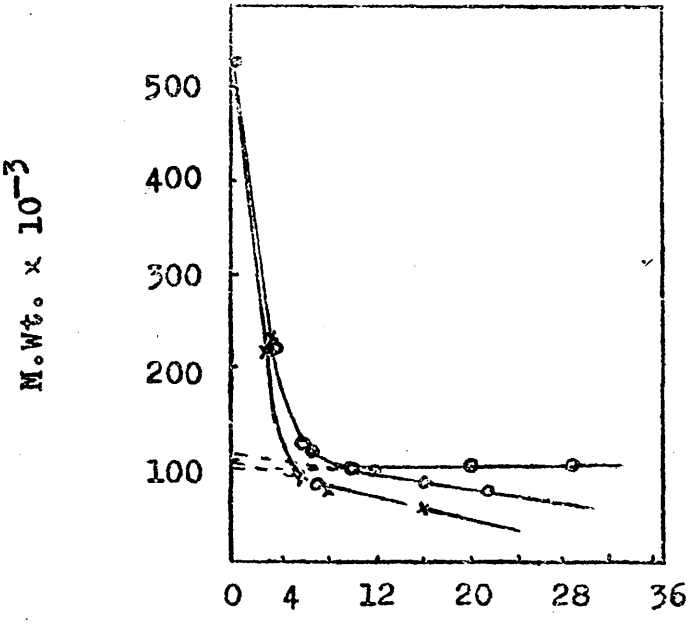
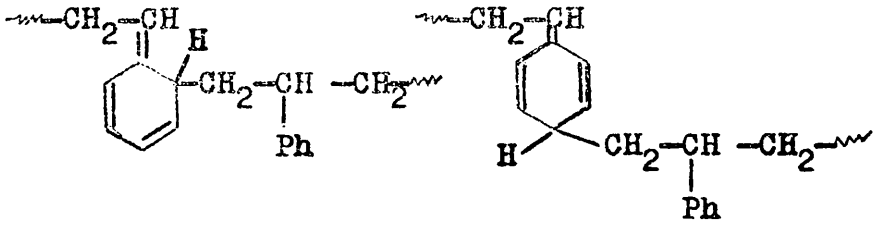


Figure 4



Molecular Weight Changes With Time Of Degradation Of Polystyrene At 325 °C In Bulk, x; In Naphthalene Solution, o; In Tetralin Solution, •.

On polymerization, these structures would give rise to:-



Thus Grassie and Kerr demonstrated weak links, while Grassie and Cameron tried to find what they are.

H. Discussion of the Weak Link and Transfer Theories of Degradation:

In favour of the weak link theory we have the results of Jellink and of Grassie et al. On the other hand the intermolecular transfer theory proposed by Simha and Wall, has been supported by theoretical work reported by a number of authors.[32,33,34,35]

The difference between these theories lies in the different modes of initiation and the admission or exclusion of intermolecular transfer.

According to Jellink, initiation takes place exclusively by the breaking of weak links which are distributed at random along the polymer chains. The production of volatile material occurs through depropagation. The rapid fall in molecular weight which occurs in the initial stages of the reaction, is therefore a function of the initiation process (the scissions of weak links) alone.

On the other hand, according to the reaction scheme suggested by Simha and Wall, which includes intermolecular transfer, the decrease in molecular weight which characterizes the reaction, should be due, not only to the initiation step, resulting in chain scissions, but also to the randomizing intermolecular transfer. This also causes a large decrease in molecular weight, since chain scissions produce radicals which might propagate the degradation reaction through intermolecular transfer.

Jellinek and Grassie stated that intermolecular transfer should result in a continuous decrease in molecular weight to values lower than those obtained experimentally. Gordon[32], however, claimed from theoretical considerations that the molecular weight values reached are quite consistent with a transfer mechanism.

Grassie and Kerr, as mentioned earlier, have given evidence that the concentration of weak links in polystyrene is a function of polymerization temperature, which provides support for the weak link theory, since if the reaction can be explained by intermolecular transfer alone, these would be expected to be independent of the polymerization process.

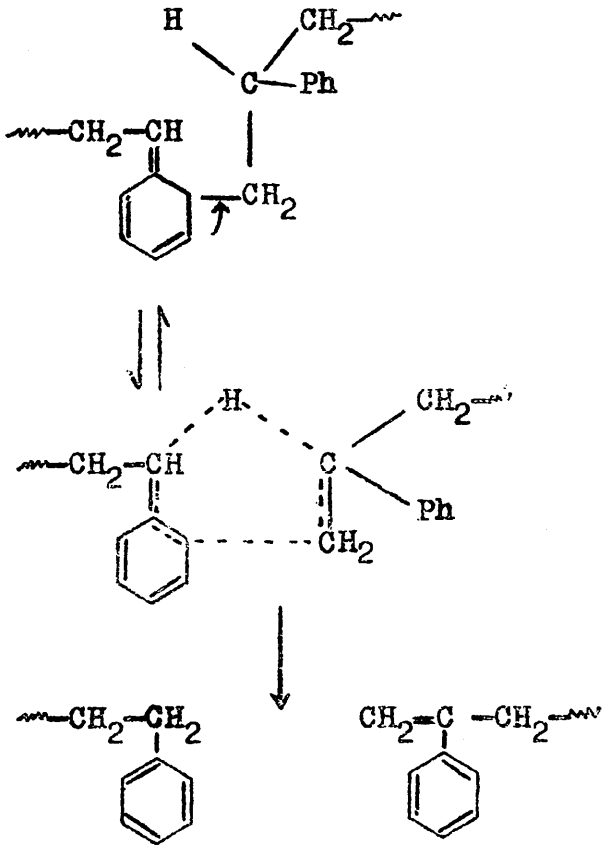
More recently, Grassie and Cameron found evidence in support of the weak link theory, as pointed out before. From their results they concluded that the initial

steep fall in molecular weight is due to weak link scissions producing non-radical products, rather than to an intermolecular transfer process. Volatile products are produced by a radical reaction initiated exclusively at chain ends. Non-monomeric volatile products, dimer to pentamer, are produced by intramolecular transfer near chain ends.

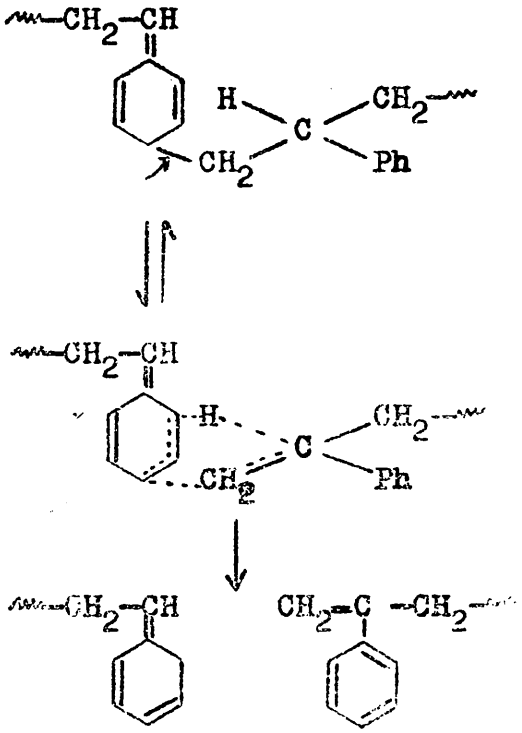
Jellinek, on the other hand, suggested that weak link scissions result in the production of radicals which depropagate to give rise to volatile material.

Grassie and Cameron, as discussed previously, based their conclusions on the experimental findings. The rate of weak link scissions in bulk polymer and in both tetralin and naphthalene solutions are the same, though the rate of evolution of volatile material is affected by the medium. This can not be explained in terms of the transfer theory which requires that volatilization and molecular weight decrease should run parallel. Grassie et al considered them two separate processes, and proposed the following reaction scheme, involving quinonoid type structures . Scissions of the weakest C-C bond, (next but one to two double bonds[36], as indicated) and also an (α) hydrogen transfer, were assumed to occur:-

Ortho type weak link:-



Para type weak link:-

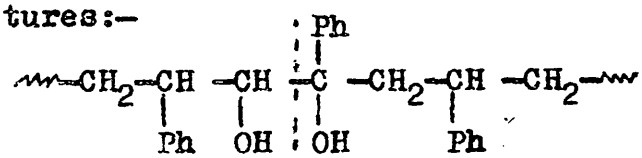


This mechanism could account for the isotope effect in the degradation of poly-γ-deutero styrene. The presence of the heavy deuterium atom would affect the rate at which the weak links are broken thermally, since transfer of the deuterium atom requires a higher energy of activation than that involving hydrogen atoms. Also the increased yield of monomer would be expected, as substitution of the tertiary hydrogen atom by deuterium would render intramolecular transfer more difficult.

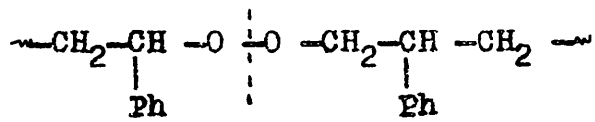
In spite of all the above evidence which supports the weak link theory, it is not generally accepted.

I. The Possible Structure of Weak Links:

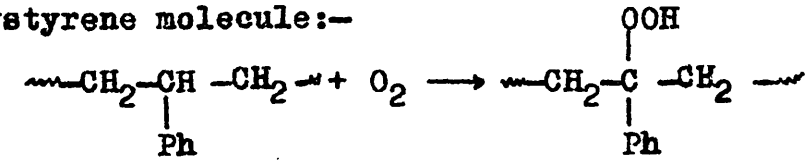
The oxygenated weak link theory of Jellinek has already been discussed. It was suggested that chain scissions in the degradation of polystyrene occurs at oxygenated structures which are formed in the polymer chains during polymerization, either in the form of hydroperoxy structures:-



or by direct incorporation of peroxide groups into the polymer chain, presumably forming a true copolymer:-



These thermo-labile oxygenated structures may also be produced by peroxidation of the tertiary hydrogen atoms in the polystyrene molecule:-



For example, during storage[1] under the influence of light and air at ordinary temperatures, or by carrying out thermal degradation of the polymer in the presence of air[14].

Achhammer, Reiny and Reinhart[37] have examined the

oxidation of polystyrene, accelerating the reaction by irradiating the polymer with ultra-violet light. The infra-red spectrum of the oxidized polymer showed the appearance of absorption bands in the 3450 cm^{-1} and 1730 cm^{-1} regions. These authors suggested that these bands are due to hydroxyl and carbonyl absorption respectively; arising from the decomposition of the hydroperoxide groups attached to carbon atoms (α) to the phenyl groups.

Weir[38] has shown that traces of peroxide in polystyrene undetectable by infra-red, are sufficient to give detectable chain scissions when the polymer is subsequently heated.

Grassie and Kerr have shown that such oxygenated structures are not the sole cause of weak links, because these are still detected in polymers prepared from carefully purified monomer, polymerized in vacuum.

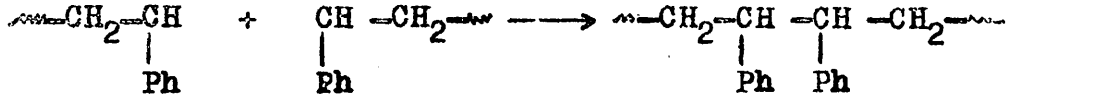
Since the polymerization conditions and the subsequent treatment can obviously affect degradation behaviour, it has been suggested[39] that this might account for certain conflicting features in the results of other workers, because much of the previous work has been done on commercial polymers.

Grassie and Kerr[28], however, showed by comparing the degradation properties of a freshly prepared polymer, with those of the same polymer after eight months of

normal laboratory storage, that normal storage conditions are unlikely to have any effect on the polymer.

These authors also found that the concentration of weak links depends only on the temperature of polymerization[29] and increases as this temperature is raised. This has been interpreted as indicating that weak links are formed in some process which competes directly with the normal propagation step (head to tail addition) in the polymerization process and which has a slightly higher energy of activation than propagation.

Branching, though reported to be negligible,[40,41] may provide another source of potential abnormalities. Grassie and Kerr showed that weak links do not result from branching process, but suggested that head to head linkages may be the cause, since it is now agreed that termination takes place during styrene polymerization by the combination of radicals.[42,43,44] Thus each polymer molecule should contain at least one head to head linkage:-

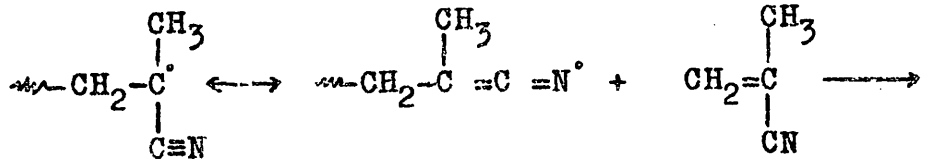


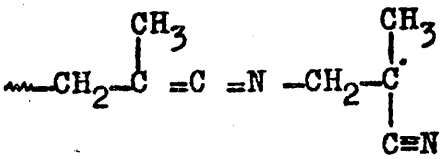
Such head to head arrangements of structural units have been detected in polyvinyl acetate[45] and polyvinylidene fluoride[46]. However, Grassie et al found that some low molecular weight polymers contained, on the average, less than one weak link per molecule.

Later, Grassie and Cameron demonstrated that head

to head structures do not constitute weak links in polystyrene and proposed that weak links are associated with unsaturation in the main polymer chains. Possibly quinonoid structures are formed as a result of polymerization through a canonical form of the benzene ring, as previously stated. By extending their studies to ionically prepared polystyrenes, thay were able to deduce that the same abnormalities are responsible for weak links in polystyrenes prepared by all three methods, namely; free radical, cationic and anionic.

This type of structure is analogous to the ketene-imine linkages which Talat-Erben and Bywater[47] have demonstrated to be present in polymeth-acrylonitrile. These linkages are formed by polymerization through a resonance form of the growing polymer radical as follows:-





This has been later confirmed by Grassie and McNeill[48] who showed that the occurence of these abnormalities is dependent upon the conditions of polymerization.

Similar observations have been made, more recently, in polyacrylonitrile.[49]

The concentrations of these structural abnormalities in polystyrene required to explain experimental results, are so low, (0.1% of monomer ~~are~~ is affected) that chemical and spectroscopic methods have failed so far to detect them. A comparison was made by Grassie[50] of the infra-red spectra of polymers before and after decomposition of weak links, but it has revealed no further evidence.

Although all this evidence represents proof that the weak links in polystyrene are associated with structural abnormalities incorporating unsaturation, it gives no further information of their chemical nature or mode of formation.

J, <u>Aim of the Present Work:</u>

One of the more likely proposals about the chemical structure of weak links in polystyrene is that suggested by Grassie and Cameron. If weak links are formed in the way suggested by these authors and have the sort of structure they proposed, which is mentioned earlier, then substitution in the ring would be expected to have a marked influence on the mode of formation and decomposition of weak links.

For this reason it was decided to study the decomposition reactions of methyl ring substituted-

styrenes and to compare them with polystyrene itself.

Before starting such work,however,it seemed that it would be useful to have as much information as possible about the detailed structure of the polymer to be degraded, since it has already been pointed out that there is a close relationship between polymerization and some degradation features.

This can most effectively be done by examination of the polymerization reaction and the determination of the rate constants of the primary processes of polymerization.This allows comparison to be made with styrene and could also contribute to the knowledge which already exists on the relationship between structure and reactivity in polymerization.

Thermal degradation studies have also been extended to "living polymers" of styrene,in order to collect as much information as possible for the investigation of the weak link theory,since these polymers appear to contain structural abnormalities.

In order to avoid,as far as possible,any confusing evidence or complications,the polymers used in this work were prepared under carefully controlled conditions, which are described in Chapter 2.Care was also taken to store these polymers away from direct sunlight.

CHAPTER 2

APPARATUS AND EXPERIMENTAL TECHNIQUES

A. Polymerization

All polymerizations were carried out in dilatometers sealed under vacuum. The reaction was followed by continuous measurements, using a cathetometer, of the decrease in level of the liquid meniscus in the stem of the dilatometer.

i. Preparation of Polymers:

i.a. Purification of Initiator:

The initiator used in this work was 2,2-azobis-isobutyronitrile (AIBN) (Eastman Kodak Ltd.). It was recrystallised from analar methanol before use; the solution having been filtered hot to remove insoluble polymeric material derived from the decomposition of initiator.

b. Purification of Monomers:

The monomers used, (Koch Laboratories), 4-methyl styrene and 2,4-dimethyl styrene contained p.-tert.-butyl catechol as inhibitor; 2,4,6-trimethyl styrene did not contain inhibitor.

Inhibitors were removed by repeated washing with

sodium hydroxide solution until the aqueous layer was colourless. After further washings with water to remove traces of alkali, the inhibitor free monomer was dried over calcium chloride and distilled under reduced pressure; the first portion of the distillate being discarded. In all cases the distillate was a colourless, water like liquid. The purified monomer was stored at $-10^{\circ}C$.

In order to calculate the extent and rate of polymerization and also monomer concentration, which is required in the evaluation of polymerization rate constants in absolute units, the cubical coefficient of thermal expansion of monomers and their density had to be obtained.

C. Coefficient of Expansion of Monomers:

The cubical coefficient of thermal expansion of monomers was measured by observing the expansion and contraction in level of a known volume of the monomer, at room temperature, with change in temperature in the range 50 to $80^{\circ}C$, in a dilatometer immersed in a large thermostat. The change in level was measured by means of a cathetometer.

The volume of monomer at a temperature t_E is given by:-

$$Vt_E = Vt_R \left[1 + \beta \ (t_E - t_R) \right]$$

Where Vt_E = volume of monomer at the experimental temperature.

Vt_R = volume of monomer at room temperature.

t_E & t_R = experimental and room temperature respectively.

β = cubical coefficient of thermal expansion.

Results are given in Table 2.

The cubical coefficient of thermal expansion of pyrex glass ($3 \times 0.036 \times 10^{-4}$) was taken into account.

Table 2

Coefficient of Expansion of Monomers (β_t) ml./°C

Temp.	Monomer ($\times 10^3$)		
t°C	4-me.styrene	2,4-dime.styrene	2,4,6-trime.styrene
25	(0.9290)	(0.8910)	(0.8542)
50	(0.9537)	0.9139	(0.8763)
60	0.9637	0.9229	0.8854
70	0.9734	0.9320	0.8936
80	(0.9832)	0.9415	0.9031
90	(0.9930)	(0.9505)	(0.9118)

d. Density of Monomers:

Density of monomers was measured over the range 50-80°C, using a pyanometer with a volume of about 25ml., constructed from pyrex glass. It had previously been calibrated with distilled water at the same temperature, using densities obtained from the International Bureau of Weights and Measures Tables. The density had been calculated by applying the equation:-

$$d_4^t = \acute{W}\, D/W$$

Where $\acute{W}$ = weight of monomer at temperature t.

W = " " water " " ".

D = density of water " " ".

and d_4^t = " " monomer " " ".

Results are quoted in Table 3.

In measurements of both density and coefficient of expansion of monomers, p.-tert.-butyl catechol was added to the freshly distilled monomer to inhibit polymerization.

Hence the monomer concentration may be calculated using the formula:-

Molar Concentration of Monomer = Density(d_4^t)x1./M.Wt. of Mon.

and the results are given in Table 4.

Table 3

Density of Monomers (d_4^t) g./ml.

Temp.	Monomer		
t °C	4-me.styrene	2,4-dime.styrene	2,4,6-trime.styrene
25	(0.8893)	(0.9037)	(0.8977)
50	0.8678	0.8824	0.8776
60	0.8592	0.8740	0.8696
70	0.8506	0.8654	0.8618
80	(0.8420)	0.8569	0.8537
90	(0.8333)	(0.8483)	(0.8457)

Values between brackets in Tables 2 and 3 were obtained by extrapolation.

Table 4

Molar Concentration of Monomers (M) g.mole/l.

Temp.	Monomer		
t°C	4-me.styrene	2,4-dime.styrene	2,4,6-trime.styrene
25	7.525	6.836	6.139
50	7.341	6.676	6.002
60	7.269	6.612	5.947
70	7.196	6.546	5.893
80	7.124	6.483	5.838
90	7.050	6.418	5.785

e. Filling of Dilatometers:

The high vacuum system used for filling dilatometers consisted of a mercury diffusion pump backed by a rotary oil pump. A vacuum of the order of 10^{-5} mm. Hg. ~~being~~ was obtained. This system and the degradation system were constructed of pyrex glass. All ground glass surfaces were lubricated with high vacuum silicone grease. For rate measurements, dilatometer bulbs were usually of 8-12ml. capacity, the stems being made from graduated tubing.

Initiator when required, was introduced into the reaction tubes in benzene solution, the solvent being removed at the water pump before distillation of the monomer was commenced. The monomer being used was placed in a storage tube and degassed under high vacuum by repeated cycles of freezing in liquid air, evacuation and thawing. About the first 5% of the monomer was distilled off and discarded. Portions were transferred by distillation at room temperature, under high vacuum, into a burette tube and measured volumes subsequently distilled into the dilatometer, after which it was sealed off under high vacuum.

In the case of vinyl mesitylene monomer, distillation at room temperature was very slow, owing to its high boiling point 209°C at 760mm. Hg. Accordingly, the monomer in both the storage and burette tubes was warmed to about 50°C. in a water bath.

Photopolymerization Techniques:

Light Sources:

For photochemical experiments the source of radiation was an osram 125 w MB type mercury arc lamp. In order to avoid "skin effects" due to non-uniform absorbtion of light by a thick layer of monomer, it was necessary to use wavelengths greater than 3200Å. This was achieved by the glass envelope, which acted as an

efficient filter removing all radiation with a wave length shorter than 3200Å.

In "rotating sector" experiments for which a sharper source of light was needed, the glass envelope was removed. The soft glass lenses used with this system served as filters. In order to minimize intensity fluctuations, the lamp had to be run for about an hour, before measurements were started.

Intensity Screens:

In order to investigate the effect of the incident light intensity on the rate of polymerization, a means of cutting down the intensity by known relative fractions was required. This was done by using several standard screens made of wire gauzes of different mesh sizes and wire gauges. Their transmission coefficient, relative to full intensity had been measured using a uranyl oxalate actinometer[51] and are as follows:-

	Full light	Screen A	Screen B	Screen C.
%Transmission	100	42.6	20.9	10.4

Rotating Sector Apparatus:

For determination of the rate constants of the polymerization process of the monomers previously mentioned, the lifetime of the growing polymer radical has to be measured. This was done by means of the rotating sector technique, the theory of which is described by Burnett and Melville[52].

The rates of polymerization were measured under different illumination conditions; full intensity and intermittent illumination,with a range of different exposure time between 0.08 of a second and 10 seconds. For flash time of longer duration,a manually operated shutter was used.The flash time was measured by observing the sector speed by means of a stop watch.

f.Polymerization:

Polymerizations were carried out in the temperature range 50–90°C ,in a water thermostat.Since dilatometers are sensitive to temperature fluctuations,it was controlled to ±0.05°C.by a Sunvic H.V.C.relay and a spiral type mercury–toluene regulator.

Polymerizations initiated by photodecomposition of initiator (AIBN),were carried out at 25°C,at which temperature the rate of thermal polymerization is negligible,in a thermostat with a silica window.For temperature control,it was found that cold water was a satisfactory coolant for 25°C.by immersing a cooling coil in the thermostat.

The expansion of monomer and its subsequent contraction on polymerization was followed by continuous measurements with the cathetometer.

g.Dilatometric Relationship:

Extent and rates of polymerization were estimated

by a relationship between decrease in volume of the polymerizing system, which occurs when the monomer is converted to the more dense polymer, and the amount of polymer produced, which is determined by precipitation and weighing, as follows:-

$$\%Sh. = \frac{V_m - V_m'}{V_m} \times 100$$

Where, %Sh. = percentage shrinkage in volume.

V_m = volume of monomer at polymerization temperature.

V_m' = volume of monomer-polymer mixture.

and the results are given in Table 5.

Consequently,

$$\%Poly. = \frac{W_p}{W_m} \times 100$$

Where, %Poly. = extent of polymerization.

W_p = weight of polymer produced.

W_m = " " monomer at polymerization temperature.

Results are quoted in Table 6.

Table 5

Percentage Shrinkage for 100% Polymerization

Temp.	Monomer %Sh		
$t^{o}C$	4-me.styrene	2,4-dime.styrene	2,4,6-trime.styrene
50	14.24	-	-
60	14.73	12.5	14.7
70	15.25	-	15.55
80	15.72	14.13	-

h. Isolation and Drying of Polymers:

Polymerizations were stopped at low conversions (10%), since at higher conversions cross linking, chain branching and other side effects may become significant.

In the preparation of polymers for measurement of rate constants, the polymer must be isolated from the reaction mixture and should be obtained free from low molecular weight impurities, particularly monomer and residual initiator. This was satisfactorily done by dissolving

the polymer-monomer mixture in analar dioxan, followed by precipitation of the polymer by pouring this solution into analar methanol. The resulting polymer was filtered off in a weighed sintered glass crucible and dried at 40-50°C in a vacuum dessicator.

ii. Molecular Weight Measurements:

The number average molecular weights of the polymers used for polymerization studies, were measured by standard methods, using the Constant Pressure Dynamic Osmometer, devised by McNeill.[53] Later, a High Speed Membrane Osmometer (Mechrolab Model 501) was used.

The membranes were "Pecel" 600 grade cellophane supplied by Polymer Consultants Limited, or "Sylvania" 300 grade cellophane. The solvent was benzene with the former osmometer and toluene with the latter.

The number average molecular weights were determined by applying the formula:-

$$\overline{Mn} = \frac{RT}{\left(\frac{\pi}{C}\right)_{C \longrightarrow 0}}$$

Where, $\overline{Mn}$ = number average molecular weight.

R = gas constant.

T = absolute temperature.

π = osmotic pressure.

and C = concentration of solution.

Some of the results obtained are given in Table 6.

Table 6 (A)

4-Methyl styrene Polymers prepared Free Radically.

Poly. Temp. $t^{o}C$	Ext.of Poly. %	Ini. Conc. $\times 10^{2}$ % W/V	M.Wt. $\times 10^{-3}$ C.P.D.O.
50	3.29	39.5	154
"	3.57	55.2	137.4
"	3.80	58.9	133.8
"	4.14	66.4	115.5
"	4.01	85.5	105.9
60	4.73	31.7	130.3
"	4.86	34.5	127.1
"	6.25	42.8	111.8
"	6.19	50.1	107.0
70	7.06	2.92	254.2
"	8.46	5.93	195.5
"	7.44	5.81	197.0
"	11.10	21.0	115.5
80	3.70	0.81	363.1
"	5.37	2.45	248.0
"	7.16	3.74	211.7
"	5.69	3.81	208.3
"	7.54	5.62	182.8
"	8.28	7.36	154.0

Table 6 (B)

2,4-Dimethyl styrene Polymers prepared Free Radically

Poly. Temp. t °C	Ext.of Poly. %	Ini. Conc. x 10^2 % W/V	M.Wt. x 10^3 C.P.D.O.
60	3.33	18.3	128.5
"	8.04	28.6	107.9
"	4.57	31.6	100.8
"	5.52	40.9	91.8
80	5.36	1.55	192.7
"	4.80	2.18	160.6
"	6.12	3.26	134.9
"	5.81	3.80	116.8
"	4.23	4.42	107.1
"	6.25	5.90	119.5
"	4.36	5.95	91.8
"	8.42	9.12	78.2

Where, Poly. Temp. = polymerization temperature.

Ext.of Poly.= extent of polymerization.

Ini. Conc. = initiator concentration. g./100 ml monomer.

M.Wt. = molecular weight.

C.P.D.O. = constant pressure dynamic osmometer.

Table 6 (C)

Vinyl mesitylene Polymers prepared Free Radically

Poly. Temp. t °C	Ext.of Poly. %	Ini. Conc. x 10^2 % W/V	M.Wt. x 10^{-3} C.P.D.O.
60	0.52	38.7	31.9
"	1.00	53.8	30.2
"	1.21	59.4	30.2
"	1.12	89.6	25.7
70	1.36	23.4	30.6
"	1.04	25.9	31.3
"	1.02	30.9	25.0
"	1.24	33.8	25.7
80	1.99	9.61	17.7
"	2.06	10.8	25.0
"	3.05	28.0	22.6
"	2.49	36.2	21.4
90	0.95	1.52	18.0
"	1.44	4.18	29.2
"	1.59	5.88	23.4
"	1.36	7.58	24.5
"	1.86	7.72	22.7
"	1.67	8.85	19.5
"	1.20	10.9	22.7

B. Degradation

1. Degradation Apparatus:

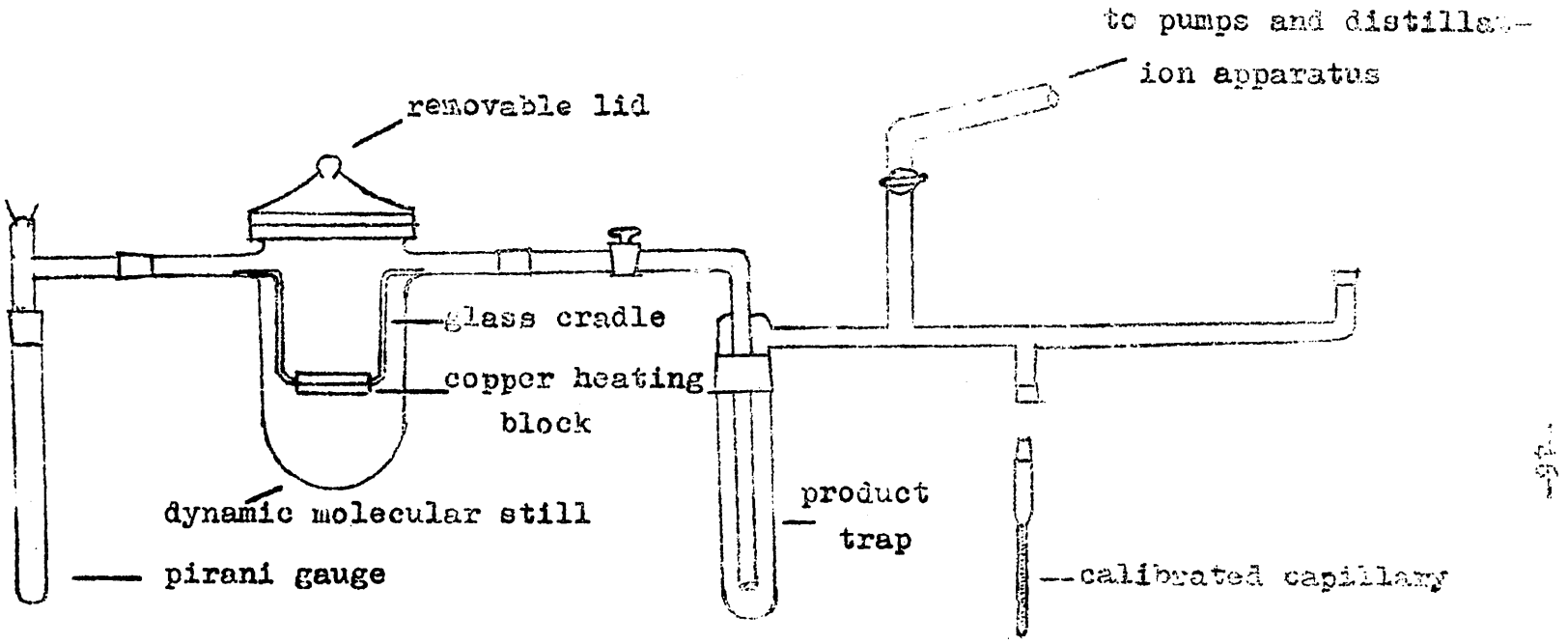
General Aspects:

All thermal degradation experiments were carried out under high vacuum, using a modified[54] form of the dynamic molecular still, developed by Grassie and Melville.[15] Fig. 5 shows the arrangement of the glass work of the degradation apparatus.

This type of system allows the polymer to be degraded in vacuum, thus avoiding the possibility of oxidative reactions. At the same time, the volatile products of the reaction are removed rapidly and effectively from the reaction zone, so that there is little possibility of their reacting further. Moreover, since in the dynamic molecular still the heated surface is separated from the cold surface (the liquid air trap), a small pressure will be built up within the still. This may be used as a measure of the rate of production of volatile material from the polymer, provided that the liquid air level is maintained constant. This pressure is measured by the pirani gauge.

a. The Dynamic Molecular Still:

The still consisted of a heavy glass cylinder, rounded at one end and closed at the other with a desicator lid on a ground glass flange. The furnace block used to



Degradation Apparatus

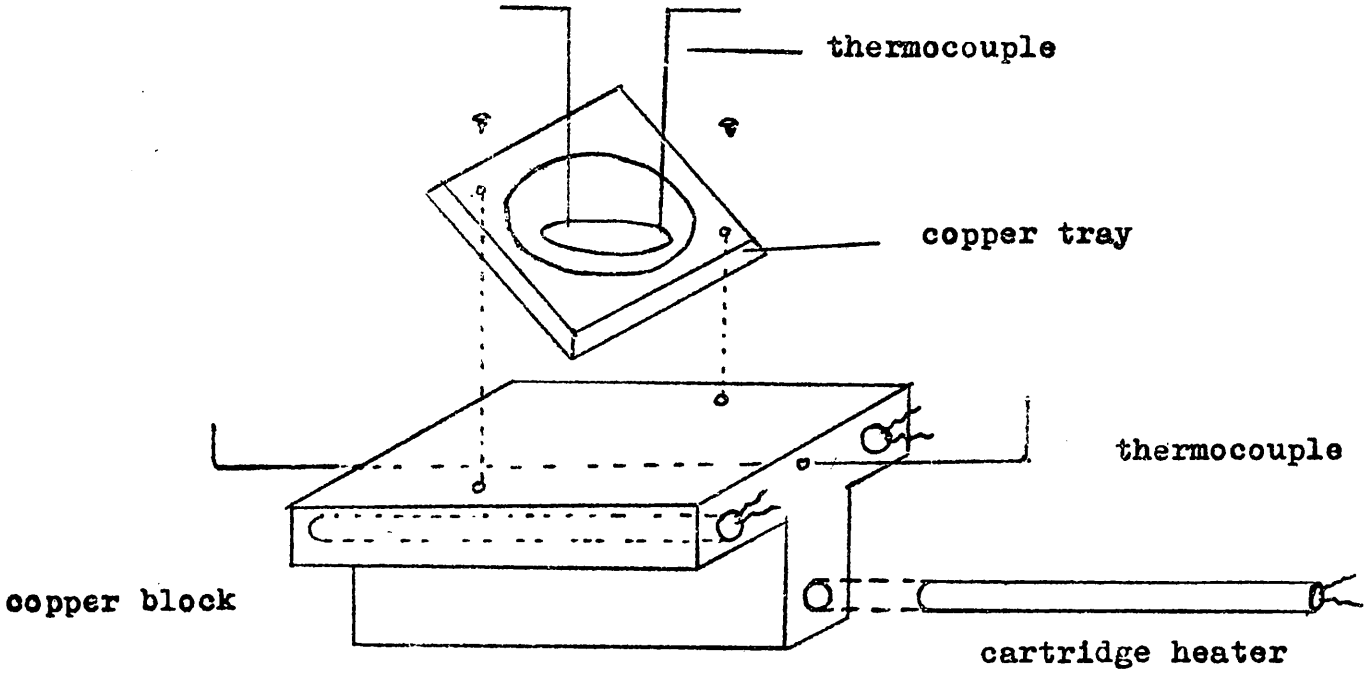
Figure 5

degrade the polymers was supported inside the still on a glass cradle.Electrical leads to and from the furnace and tray were led into the still through pieces of capillary tubing and sealed with picein wax.

b.Furnace Construction and Control:

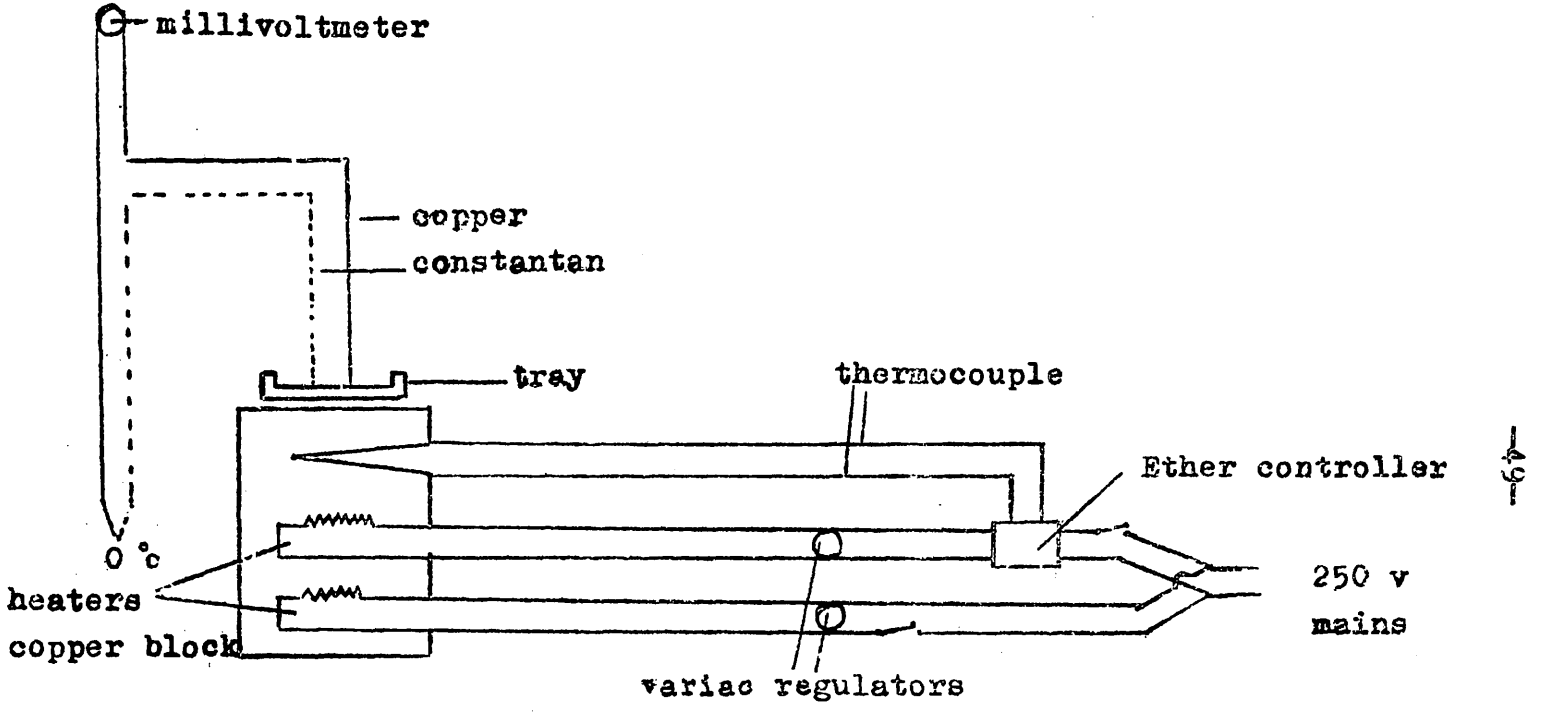
The copper furnace block and degradation tray are shown in Fig.6.The copper block was heated by three 50W 24V Cartridge heaters,which were inserted into holes drilled through the block.The upper two heaters were connected in series. During an experiment,their heat out put was constant,while the lower heater provided control by its intermittent action,by means of an Ether Transitrol Temperature Controller.This in turn was activated by a copper constantan thermocouple,housed in the copper block in a small hole drilled above the two constant heaters.

The signal from the thermocouple was passed to the controller which in turn switched on or off the intermittent heater as the thermocouple signal dictated. The voltage across the heaters was controlled by two variac voltage regulators,supplied from the mains.The electrical circuit for the heating system is shown in Fig.7 With this system,the temperature could be controlled to $\pm$ 0.5^{o}C.



Copper Furnace Block

Figure 6



Heating, Temperature Measurements And Control Circuits

Figure 7

c. The Degradation Tray:

This consisted of a copper tray with a circular cavity as shown in Fig. 6. The tray and the block were screwed firmly together before each experiment to ensure good thermal contact.

The required weight of the polymer (0.1–0.3g) was placed on the tray as a fine powder, which was covered by a layer of (60–80 mesh) copper powder (10–12g.) to ensure uniform heating and to eliminate sputtering in the sample.

The temperature of the tray was measured by a copper constantan thermocouple, silver-soldered to the surface of the cavity. The thermocouple leads were led to a millivoltmeter which had been calibrated against a standard thermometer immersed in a silicone oil bath with the tray and leads ~~which were~~ of the same resistance.

d. The Pirani Gauge:

The pirani gauge and its circuit are shown in Figs. 8 and 9 respectively. It consisted basically of an extended piece of tungsten filament 50Ω, supported between two copper wires and was attached to the still through a B24 cone.

Pressure measurements by means of a pirani gauge are based on the relationship between the thermal conductivity of a gas and its pressure.[55,56] An increase of pressure increases the number of gas molecules colliding with the hot filament and causes it to cool (by conduction of heat

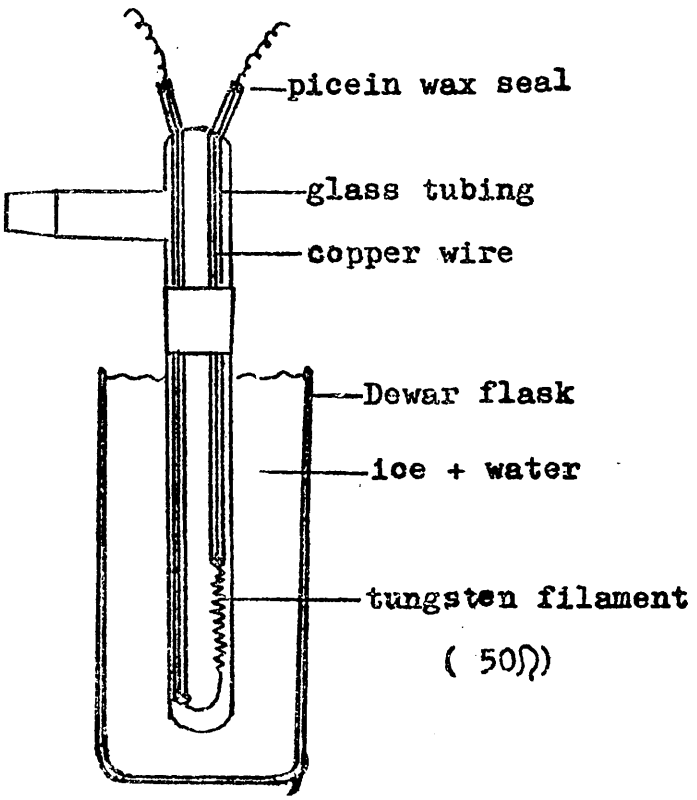
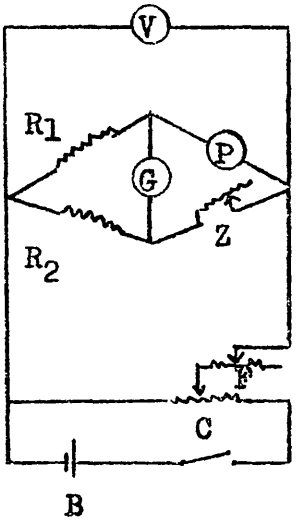


Figure 8

The Thermostated Pirani Gauge

Figure 9

Pirani Gauge Circuit



B = battery, 2 volts.

C = coarse potentiometer, 0-250 ohms.

F = fine " , 0-10 "

Z = zero control , 0-50 "

V = voltmeter , 2 volts.

G = Pye spot galvanometer.

P = pirani gauge.

R_1&R_2 = fixed resistance.

away from the wire), that is to say, lowers the temperature and thus decreases its resistance. Consequently, the bridge goes out of balance. In order to rebalance the bridge a greater voltage must therefore be applied.

The pressure at any instant in the still is proportional to the rate of volatilization[57] as follows:-

$$\frac{V^2 - V_o^2}{V_o^2} = \frac{K_3}{K_2} f(P)$$

Where, V_o = the corresponding initial voltage when the system is evacuated.

V = the voltage across the bridge when balanced at any pressure.

K_3 & K_2 = constants, depending on the nature of the gas.

f = function of pressure.

P = pressure.

Up to a pressure of 0.1mm.Hg. a linear relationship between rate of volatilization and the expression $\frac{V^2 - V_o^2}{V_o^2}$ should be obtained.

During experiments, it is necessary to have the gauge thermostated, for convenience at 0°C, in an ice-water mixture in order to eliminate effects due to change in ambient temperature, by having the external heat loss constant.

For quantitative work the gauge must be calibrated with the material responsible for the pressure change. In the present work, as the gauge was only required to determine the extent of volatilization at which the maximum rate of reaction occured, such calibration was unnecessary and the voltage was thus used to give a relative measure of the pressure in the still.

ii. Preparation of Polymers:

Polymers used for degradation studies were prepared using the technique described earlier for polymerization purposes, except that larger dilatometers of 40-50ml. capacity were used.

Moreover, for degradation experiments, the polymer was required in the form of a fine powder in order to achieve uniform heating of the sample and to enable the volatile material produced in the reaction to escape from the polymer without side reaction taking place. With larger particles the rate of the reaction might depend upon grain size.[15]

This was achieved by dissolving the polymer-monomer mixture in an excess of analar chloroform and the resulting solution was filtered and passed dropwise via a separating funnel into analar methanol which was agitated by an electric stirrer. On standing, the polymer particles settled and were filtered off after decantation of the

supernatant liquid. This process was repeated once again. The polymer was allowed to dry under a water pump and then in a vacuum desicator and finally dried in the high vacuum system.

Details of the polymers used for degradation studies are given in Table 7.

Table 7

Polymer	Temp.of Poly. ^{o}C	Ini.	Ini.Conc. x 10^{2} % W/V	Mode of Prep.	Ext. of Poly. %	M.Wt. x 10^{-3}
S_1	-	Na-Naph.	-	Anionic	-	255
S_2	-	"	-	"	-	495
S_3	-	"	-	"	-	611
S_4	60	-	-	Free R.	21	5,000
PMS_1	"	AIBN	13	"	15	138
PMS_2	120	-	-	"	10	245
PMS_3	-	-	-	"	-	420
MMS	60	AIBN	6.6	"	15	246
OMS	"	"	3.6	"	7	160
2,4/Di.MS.	80	"	5.9	"	6	119.5
2,5/Di.MS	60	"	3.7	"	6	231
2,4,6/Tri.MS	124	"	4.0	"	2	20

Polymers PMS_3 & S_4 and S_1, S_2 & S_3 were kindly supplied by Dr.Grassie and Mr. Richards, E.R.D.E. respectively.

iii .Operating Technique - The Efficiency of the Heaters:

In problems,where rate measurements are made,it is essential that the temperature of the degradation reaction should not only be maintained constant but also rapidly attained. Particularly in cases where the reaction takes place at a significant rate at temperatures below these at which measurements are to be made.

With the system described above,because of the bulk of the heating block 350g. about 20-25 minutes were required for the tray and polymer to reach the degradation temperature 330°C.

The weighed copper tray with its weighed contents (polymer + copper) was screwed to the copper heating block and connected to the thermocouple leads. The system had to be evacuated for sometime before a V_0 pirani reading was obtained. At a vacuum of 10^{-5}-10^{-6}mm.Hg. the product trap was immersed in liquid air,then the pirani bridge was balanced to zero pressure.

To raise the temperature to that required for degradation,the following technique was found to be satisfactory,between preventing overshooting and speedy attainment of the temperature:-

Initially,the temperature was raised rapidly by passing about 30 volts through the constant heaters,until the temperature was about 20°C. below the required

degradation temperature. Then it was reduced nearly to zero,so that the approach to degradation temperature was slow. Just as the degradation temperature was nearly reached,a low voltage (18-22) ,according to the required temperature,was applied which was maintained constant during the degradation run. The intermittent heater was kept on 10 V.both during the temperature rising and degradation stages. After some initial fluctuations of $\pm 1^{o}C$ it remained constant to that of the limits of detectable temperature change $\pm 0.5\ ^{o}C$ throughout the degradation run.

Before examination of the products,the system was usually left to cool over night under vacuum.

iv.Back Ground Products:

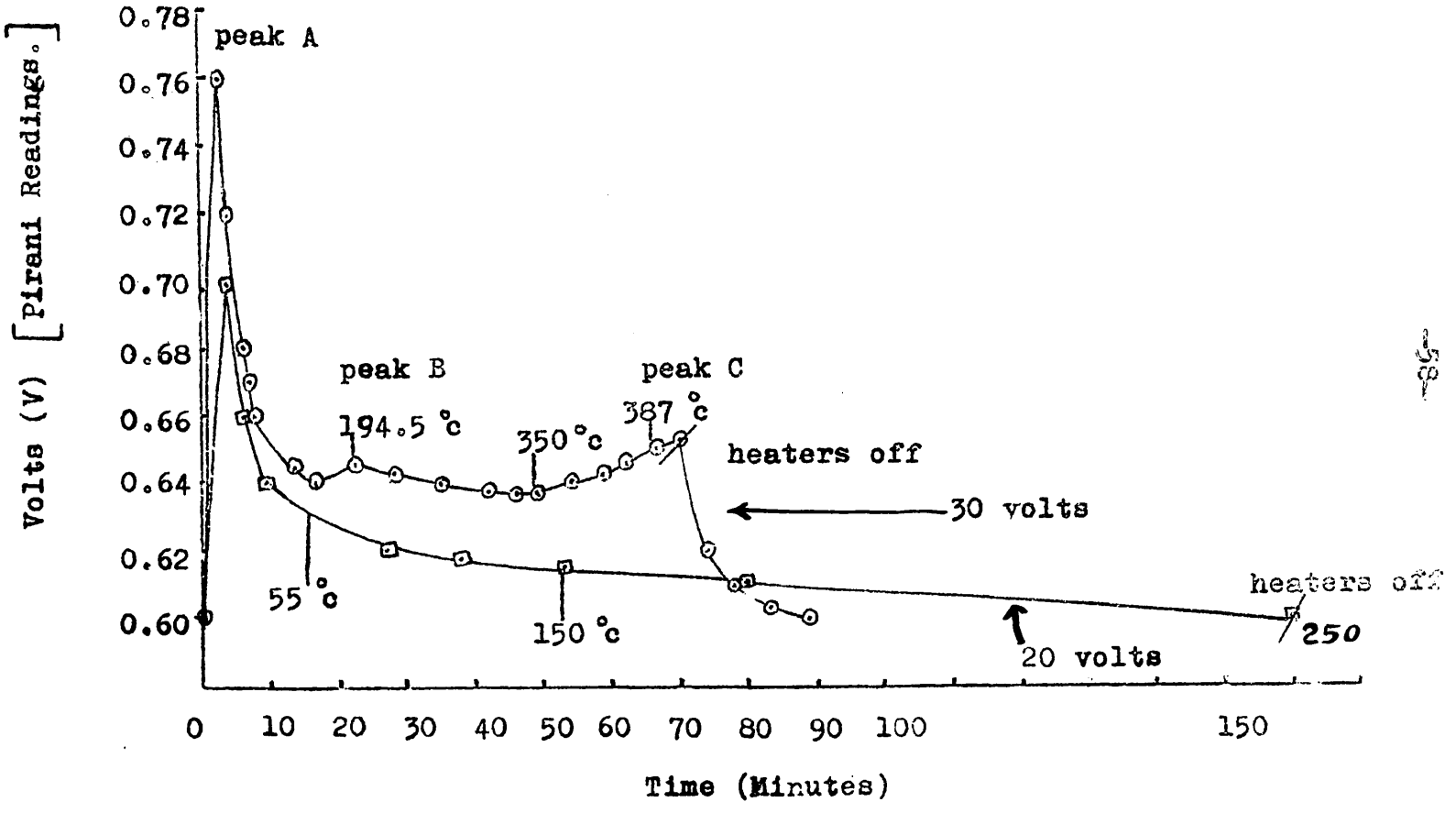
Even in the absence of polymer,volatiles were detectable in the early stages of heating. A "back ground" pirani curve is shown in Fig.10.

The first maximum peak A,in the rate of evolution of volatile material,occured immediately power was switched on and was reached before there was any appreciable change in the tray temperature. It seemed likely that these volatiles were produced from the porcelain of the cartridge heaters.

The temperature at which peak B occured was such that it could be due to gases adsorbed in several parts

Figure 10

Blank Degradation "Back Ground Volatiles"



of the still.

At higher temperature (above 350 °C) volatile products arise again, which could be due to volatiles from picein wax and high vacuum silicone grease joints.

v. Temperature Range employed in Degradation Experiments:

The temperature range chosen for thermal degradation studies was 330-350 °C (see Figs.11 and 12.) ,as this allowed the rapid fall in molecular weight during the initial stages of the reaction to be conveneintly followed, while allowing a large extent of volatilization to be reached in a reasonable time.

For example, P.-methyl styrene polymer started to degrade at approximately 270 °C as illustrated in Fig.11. Fig.13. shows that the polymer had been degrading at a reduced rate for about 5 to 6 minutes before the reaction temperature was reached. Any error introduced during this period or the corresponding cool-down period,were however negligible in relation to the periods of degradation.

vi. Measurement of Initial Rate of Degradation:

The polymer as prepared usually contained traces of volatile materials in the form of solvent and precipitant as can be seen from Fig.11. (peak B),which are evolved when the polymer begins to soften,in addition to gases adsorbed in several parts of the still,as previously mentioned.But as this was generally about 1% by weight,

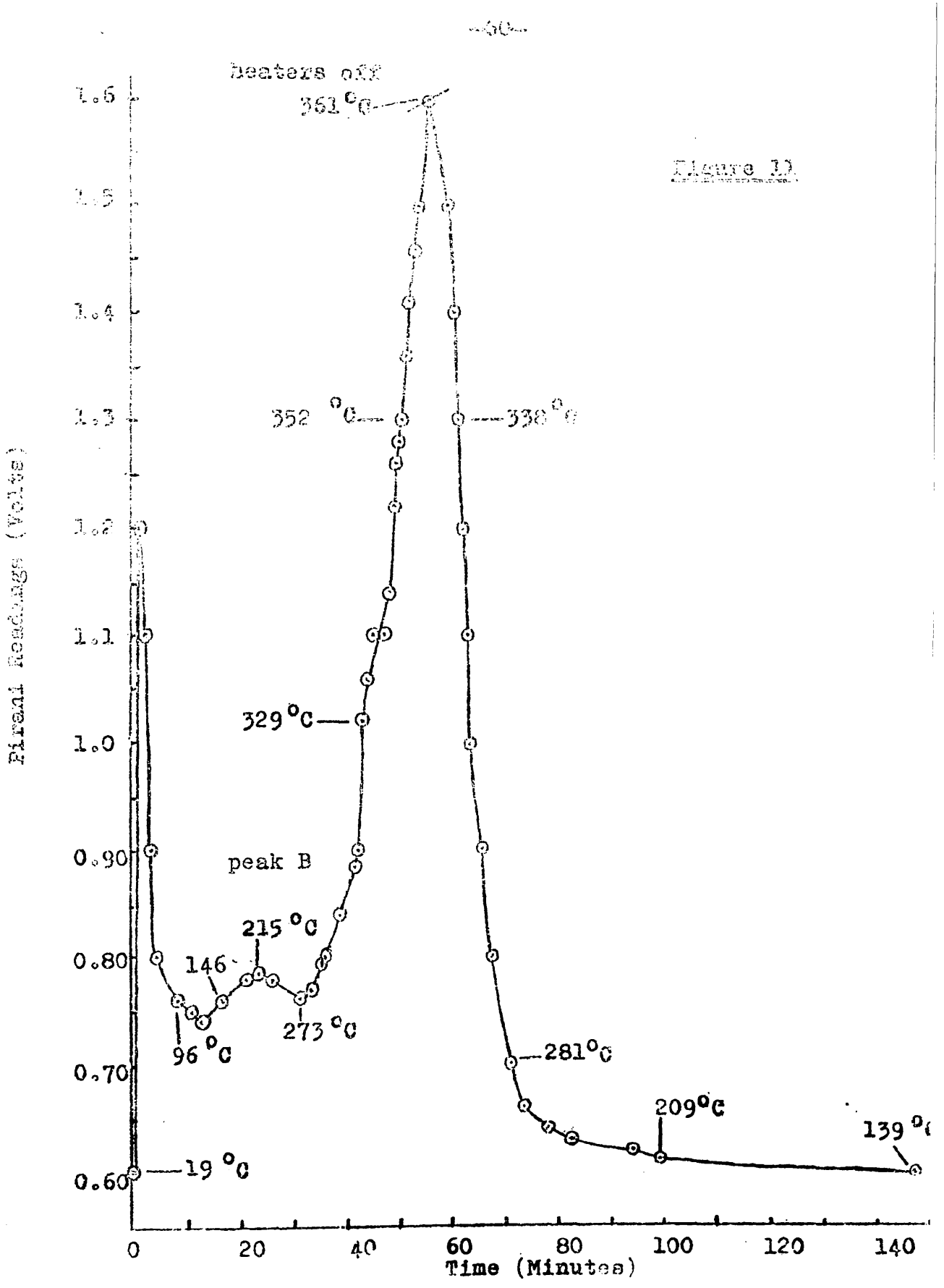

heaters off
351 °C
352 °C
338 °C
329 °C
peak B
215 °C
146
96 °C
273 °C
281°C
209°C
139 °C
19 °C
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.90
0.80
0.70
0.60
Pirani Readings (Volts)
0
20
40
60
80
100
120
140
Time (Minutes)

Figure 1)

Figure 12

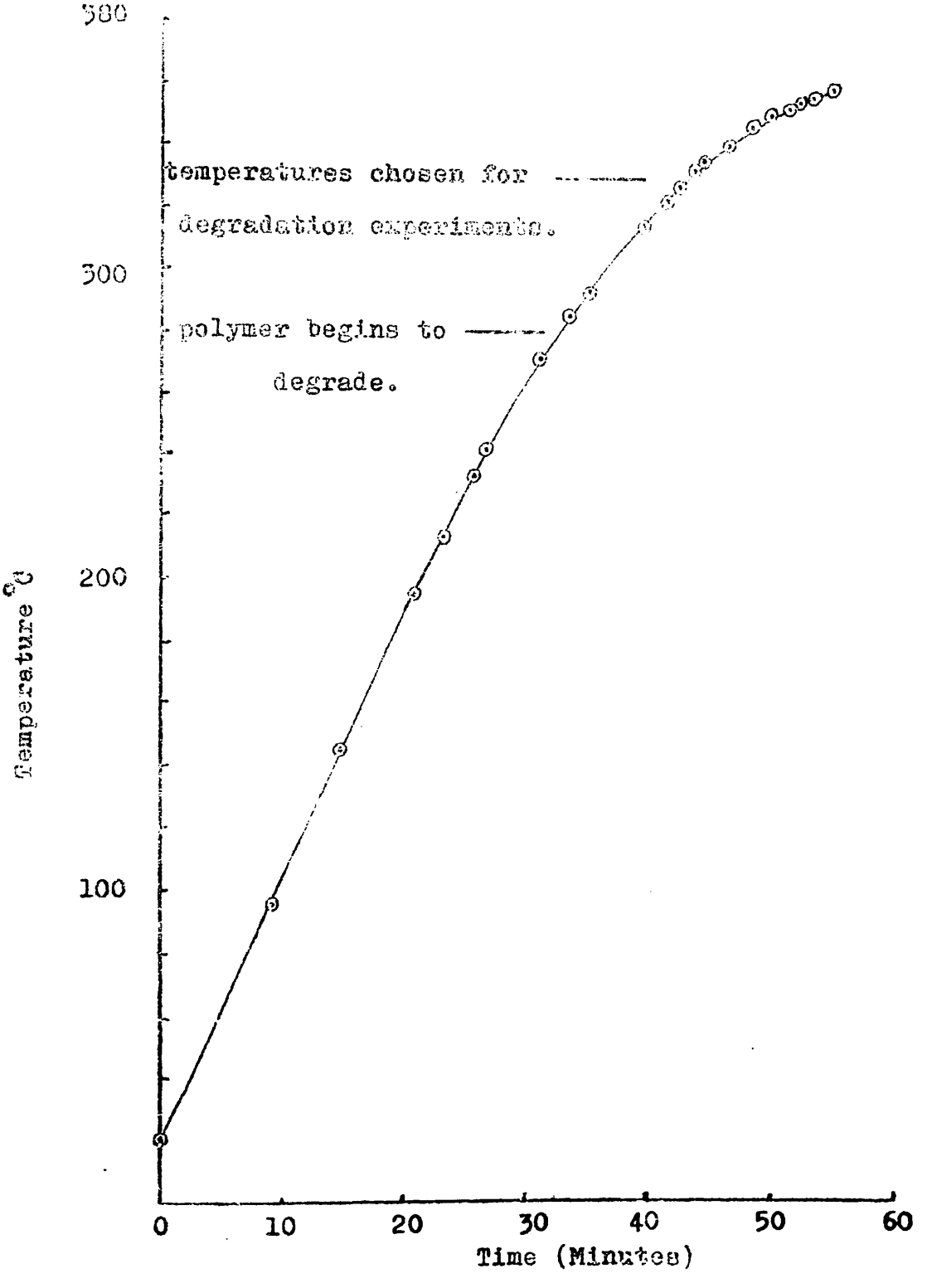
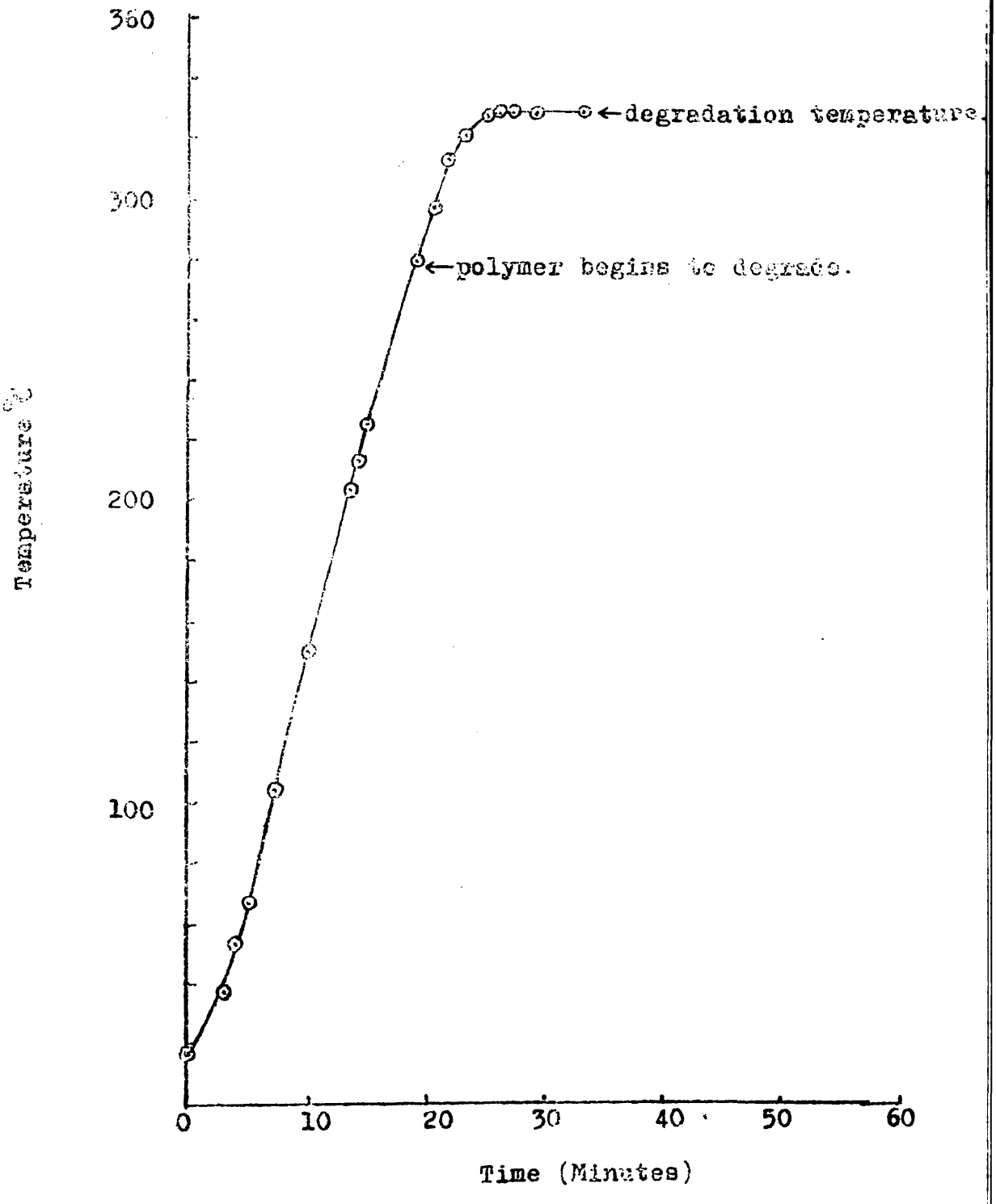

380
300
200
100
temperatures chosen for
degradation experiments.
polymer begins to
degrade.
Temperature °C
0
10
20
30
40
50
60
Time (Minutes)

Figure 13

Rate Of Heating Of Furnace



therefore, within the experimental error of the degradation experiments, it was not normally taken into account.

In order to measure the initial rate of degradation, it was necessary to eliminate these volatile materials. This was satisfactorily done by heating the polymer to 220°C and maintaining it at that temperature till the pirani voltage indicated that all the volatiles had been removed. Afterwards, the temperature was raised rapidly to the degradation temperature and the rate of volatilization followed at that temperature.

The difference in weight of the tray before and after heating gave a measure of the volatile products.

vii. Estimation of Extent of Volatilization:

The conversion of polymer to volatile material during degradation was obtained by weighing the tray and contents before and after heating.

viii. Molecular Weight Measurements:

In the case of polymers which had been degraded, the polymer residue was extracted from the copper tray by allowing it to dissolve overnight with the required solvent (toluene A.R.) at room temperature. The solution was then filtered and made up to 10 to 15ml. in a graduated flask. 1-2ml. had to be withdrawn from the solution to determine its concentration by evaporation.

In some cases, chloroform was used as a solvent,

in which case it was removed from the degraded polymer solution by evaporation in the vacuum system using the oil pump only. The polymer was then dried at 40–50 °C in the vacuum oven, weighed, then made up to 10 to 15ml. and reweighed.

Molecular weights were measured using the High Speed Membrane Osmometer.

x. Estimation of Volatile Products:

Volatile material produced during degradation in the still, was condensed in the liquid air trap. The amount of material collected was then estimated by distillation, under vacuum, at room temperature, into a capillary tube.

xi. Investigation of Volatile Products:

The volatile products of degradation were examined by vapour phase chromatography (V.P.C.).

Chromatograms were run on a Griffin and George Mark 2, and Pye argon apparatus. A sample was introduced via a syringe through a serum cap. Columns were packed with 25% APL. and operated at 100 to 125 °C. Standard samples were run under the same conditions of column packing and temperature.

xii. Linear Temperature Programmer Degradation Apparatus:

A few degradation experiments were performed on the Linear Temperature Programmer, devised by McNeill.[58] The polymer was also degraded under vacuum. The rate of

heating of the polymer, which is linear with time, could be adjusted as desired. For the present work, the rate chosen was $10^{o}C$/minute; which meant that complete degradation could be achieved in about one hour.

As little as 25m.g. of the polymer was placed in a cylindrical tube, which is surrounded by a precision oven, with a temperature range up to $500^{o}C$. The sample tube is connected to a pirani gauge and to the pumping system via flange joints. The oven is provided with a heating element and a fan which not only improves heating performance, but also enables fast cooling down rates to be achieved, when the door at the rear of the oven is opened.

Evolution of volatiles is detected by the pirani gauge, the output from which is fed to a chart recorder.

Results obtained will be discussed in a later Chapter.

CHAPTER 3

FREE RADICAL BULK POLYMERIZATION OF METHYL RING SUBSTITUTED STYRENES.

A. Introduction:

It has been pointed out in Chapter 1 that while a great deal is known about the nature of the weak links in polystyrene and the way in which they are formed during the polymerization process, their structure is not known with absolute certainty.

It was suggested however, that most of their known features could be accounted for by assuming that the polystyryl radical occasionally reacted in one of its alternative canonical forms with the radical center on the benzene ring. If this were so, then it is to be expected that the proportion of weak links would be different in ring-substituted styrenes.

However, before studying the degradation reactions in such polymers, it is important to know as much as possible about their structure and a certain amount of this kind of information can be derived from a study of the kinetics of the polymerization process.

Also a knowledge of the polymerization rate

constants could be useful in any investigation of the correlation between the chemical structure of radicals and monomers and their reactivity.

While theoretical studies can be used to predict the effect of structure on reactivity, experimental data are necessary to provide a sound basis for these predictions.

Thus, the purpose of the work described in this Chapter is to determine the individual rate constants of the various steps of the polymerization process of some methyl ring-substituted styrenes and to evaluate, if possible, the effect of substitution on the reactivity of the styrene monomer.

B. Polymerization Studies:

1. Variation of Rate of Polymerization with Initiator Concentration:

a. Thermal Catalysed Polymerization:

The effect of concentration of the initiator (AIBN) on the rate of bulk polymerization of methyl ring-substituted styrenes, namely, P.-methyl styrene, 2,4-dimethyl styrene and vinyl mesitylene, was studied over the temperature range 50° to 90° C.

The experimental results are summarized in Table 8 and illustrated in Fig.14 , which is a logarithmic plot of the rate of polymerization against initiator concentration. Results obtained for styrene at 60°C are included.

In case of styrene, 4-methyl styrene and 2,4-dimethyl styrene monomers, a linear plot is obtained which has a slope close to 0.5, showing that the rate of polymerization is proportional to the square root of the initiator concentration, over the initiator concentration range studied (0.49 to 56) 10^{-3} mole/l. monomer, and monomer concentration (5.5 to 8.5) mole/l. The catalyst exponent for 2,4,6-trimethyl styrene is abnormally low.

Table 8 (A)

Polymerization Data for Styrene.

Rate of Poly. mole/l.sec.x10^5	Ini. Conc. mole/l.x10^2	Exponent
7.8	1.17	0.5
10.9	2.44	
15.1	4.42	
16.8	5.63	

Table 8 (B)

Polymerization Data for P.-Methyl styrene.

Poly. Temp. $t^{o}C$	Rate of Poly. mole/l.sec.x10^{5}	Ini. Conc. mole/l.x10^{2}	Exponent
50	3.54	2.40	
"	4.08	3.36	
"	4.13	3.59	0.5
"	4.75	4.04	
"	5.31	5.21	
60	8.16	1.93	
"	8.57	2.10	0.51
"	9.7	2.60	
"	10.41	3.05	
70	6.29	0.178	
"	9.08	0.361	0.49
"	9.23	0.354	
"	17.0	1.28	
80	7.59	0.049	
"	12.60	0.126	
"	14.91	0.149	
"	17.46	0.229	0.505
"	17.44	0.232	
"	21.97	0.343	
"	25.79	0.448	

Table 8 (C)

Polymerization Data for 2,4-Dimethyl styrene.

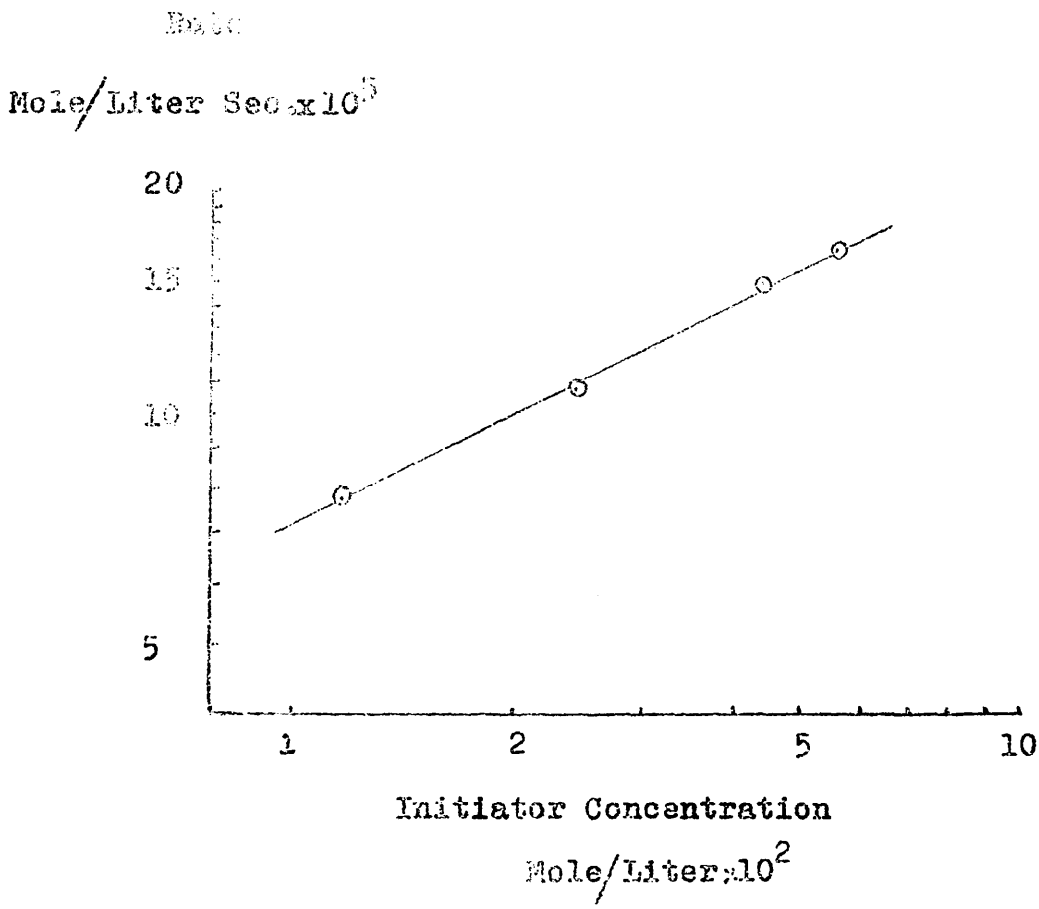
Poly.Temp. t °C	Rate of Poly. mole/l.sec.x10^5	Ini. Conc. mole/l.x10^2	Exponent
60	3.61	1.12	
"	4.54	1.74	0.49
"	4.86	1.93	
"	5.18	2.49	
80	5.74	0.0947	
"	7.71	0.133	
"	8.03	0.198	
"	9.38	0.231	0.51
"	11.08	0.269	
"	11.65	0.359	
"	14.22	0.362	
"	16.70	0.555	

Table 8 (D)

Polymerization Data for Vinyl mesitylene.

Poly.Temp. t°C	Rate of Poly. mole/l.sec.x10^5	Ini. Conc. mole/l.x10^2	Exponent
60	0.396	2.36	
"	0.436	3.28	0.31
"	0.457	3.62	
"	0.494	5.46	
70	0.749	1.43	
"	0.752	1.58	0.35
"	0.803	1.88	
"	0.850	2.06	
80	0.860	0.128	
"	1.46	0.717	
"	1.60	0.864	0.30
"	1.58	1.12	
"	1.62	1.11	
90	2.09	0.254	
"	2.51	0.358	
"	2.63	0.470	0.36
"	2.85	0.539	
"	2.94	0.662	

Figure 24 (A)



Logarithmic Plot Of Rate Of Polymerization Of Styrene Against Initiator Concentration.

Figure 14 (B)

Logarithmic Plot Of Rate Of Polymerization Of P.-Methyl styrene Against Initiator Concentration.

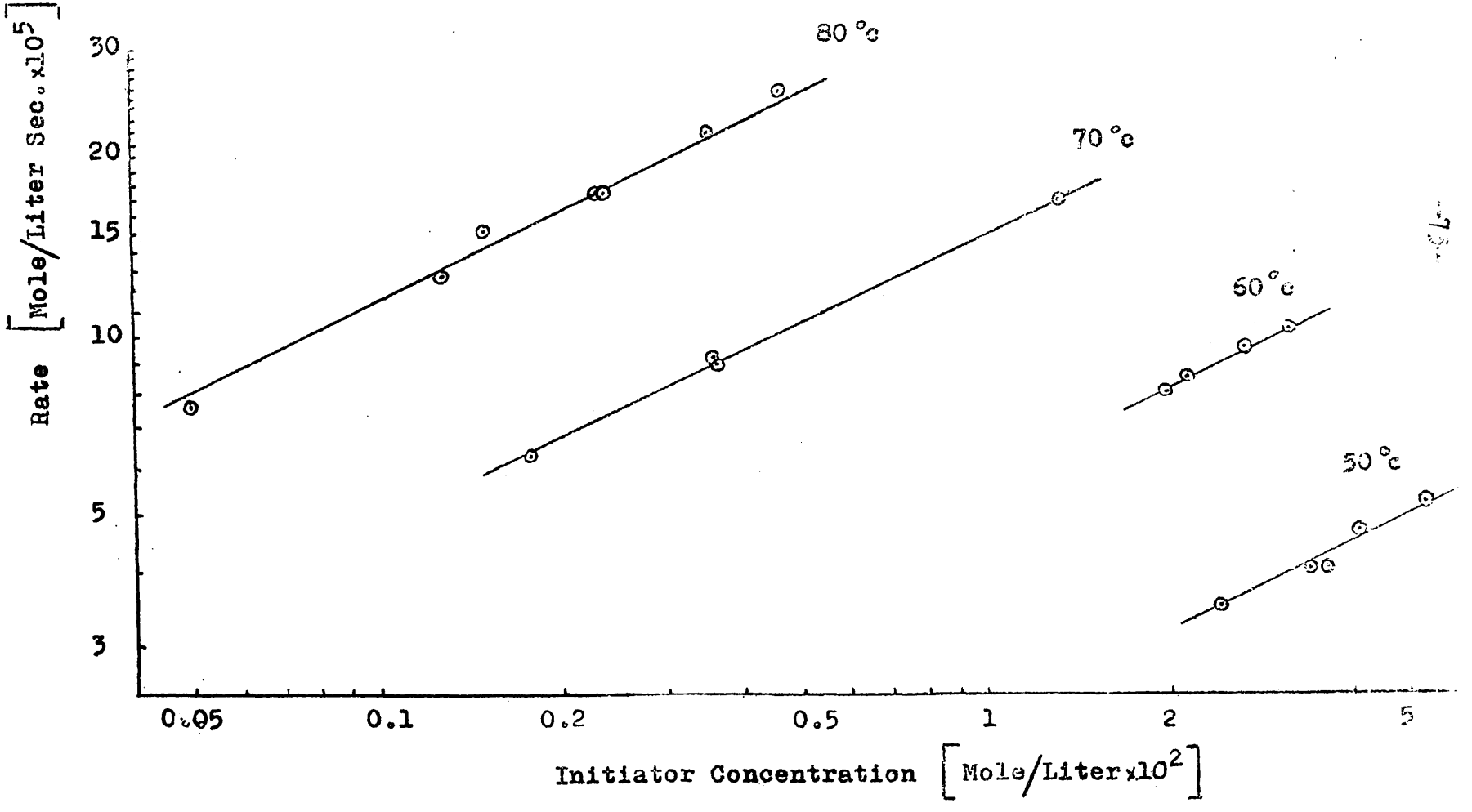


Figure 14 (C)

Logarithmic Plot Of Rate Of Polymerization Of 2,4-Dimethyl styrene Against Initiator Concentration.

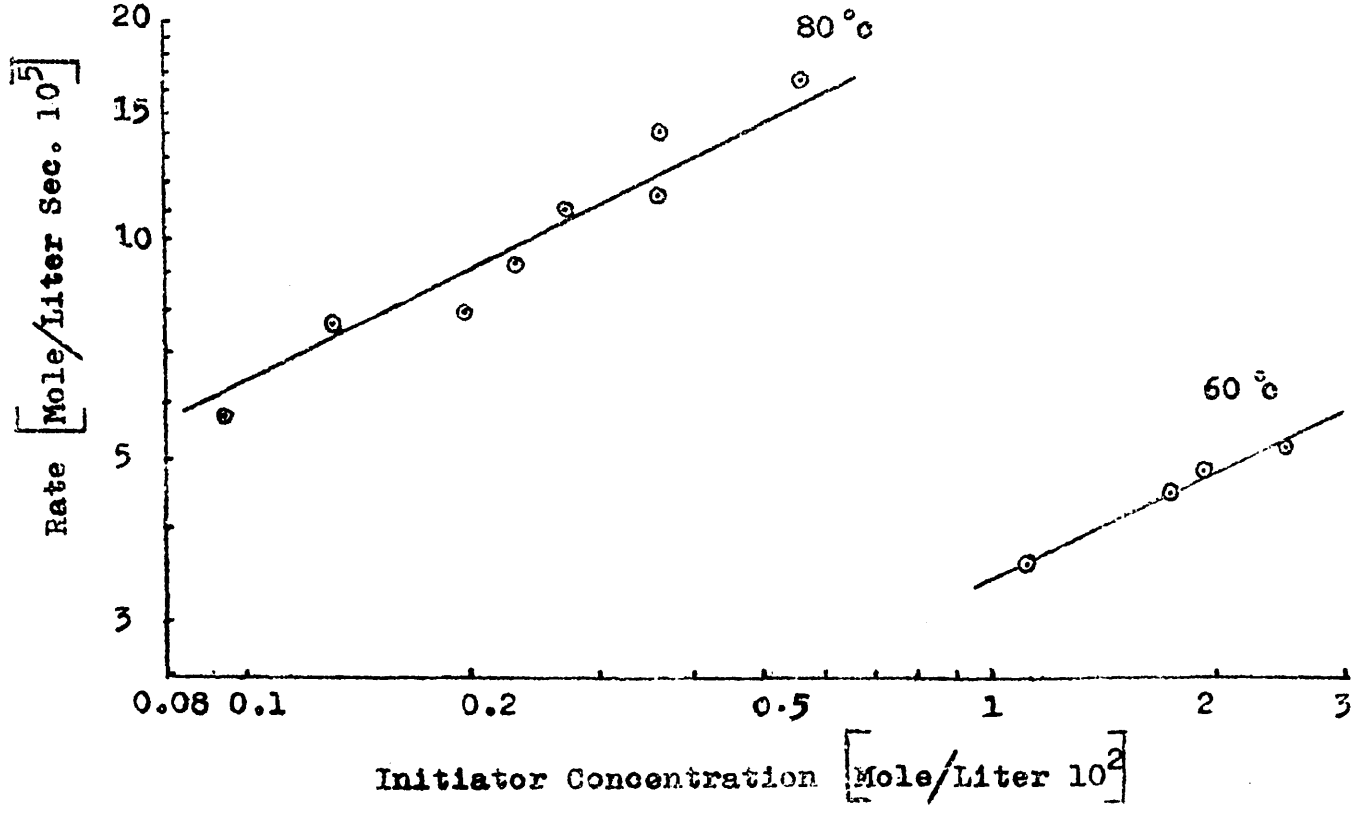
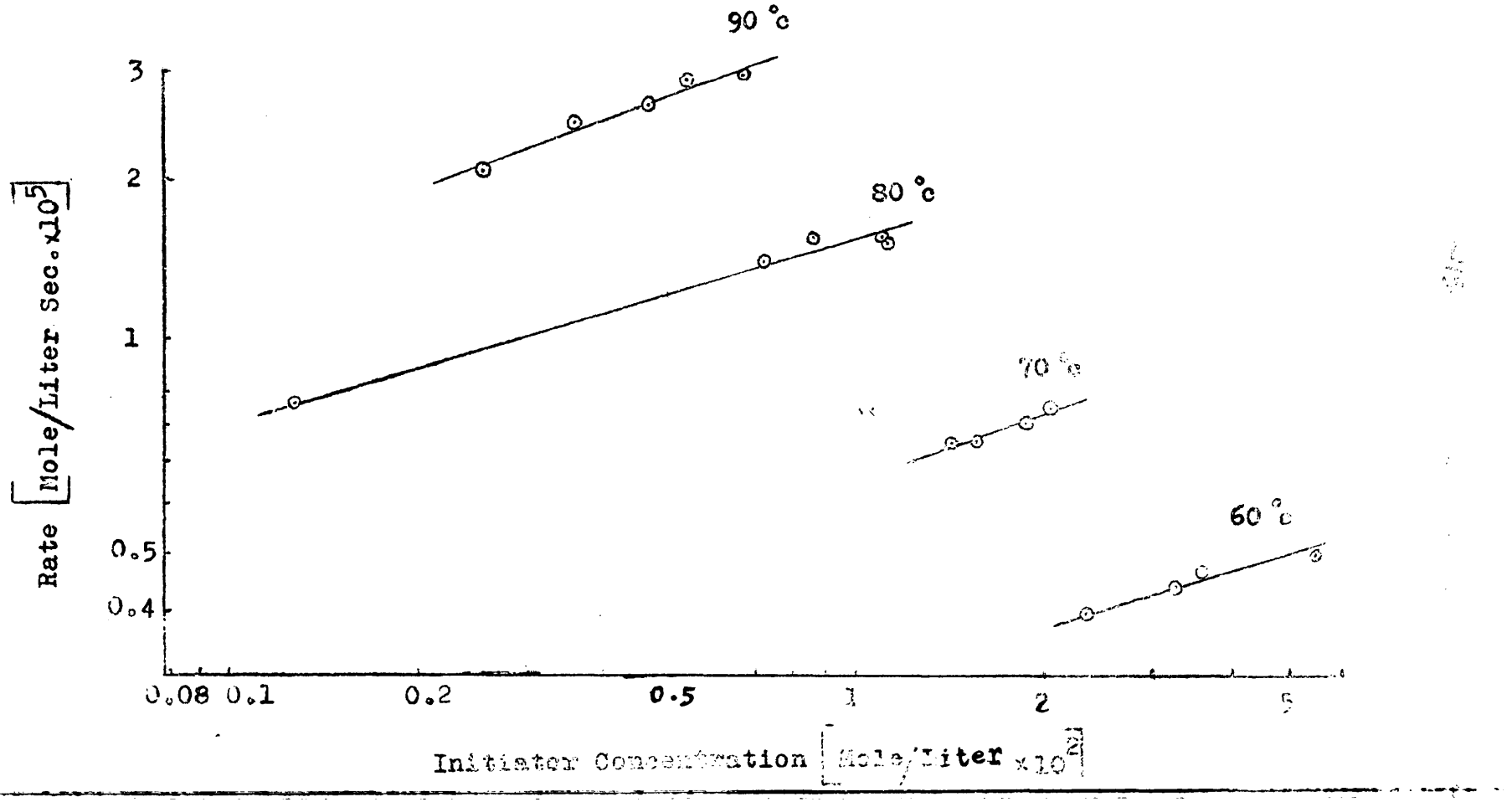


Figure 14 (D)

Logarithmic Plot Of Rate Of Polymerization Of Vinyl Mesitylene Against Initiator Concentration.



b. Photo-sensitized polymerization:

Photosensitized polymerization was studied at 25 °C. The results obtained are quoted in Table 9. and illustrated in Figs.15 and 16. which show that the sensitizer concentration and intensity exponents tend to be rather lower than 0.5. An initiator exponent less than 0.5 may indicate that while most of the termination is by reaction of pairs of molecules, termination by primary radicals[59] takes place to some small extent.

Attempts were made to measure the rate of the photosensitized polymerization of vinylmesitylene at 25 °C, but it was too low for accurate measurement using the dilatometric technique.

Table 9 (A)

Change of Polymerization Rate with Sensitizer Concentration.

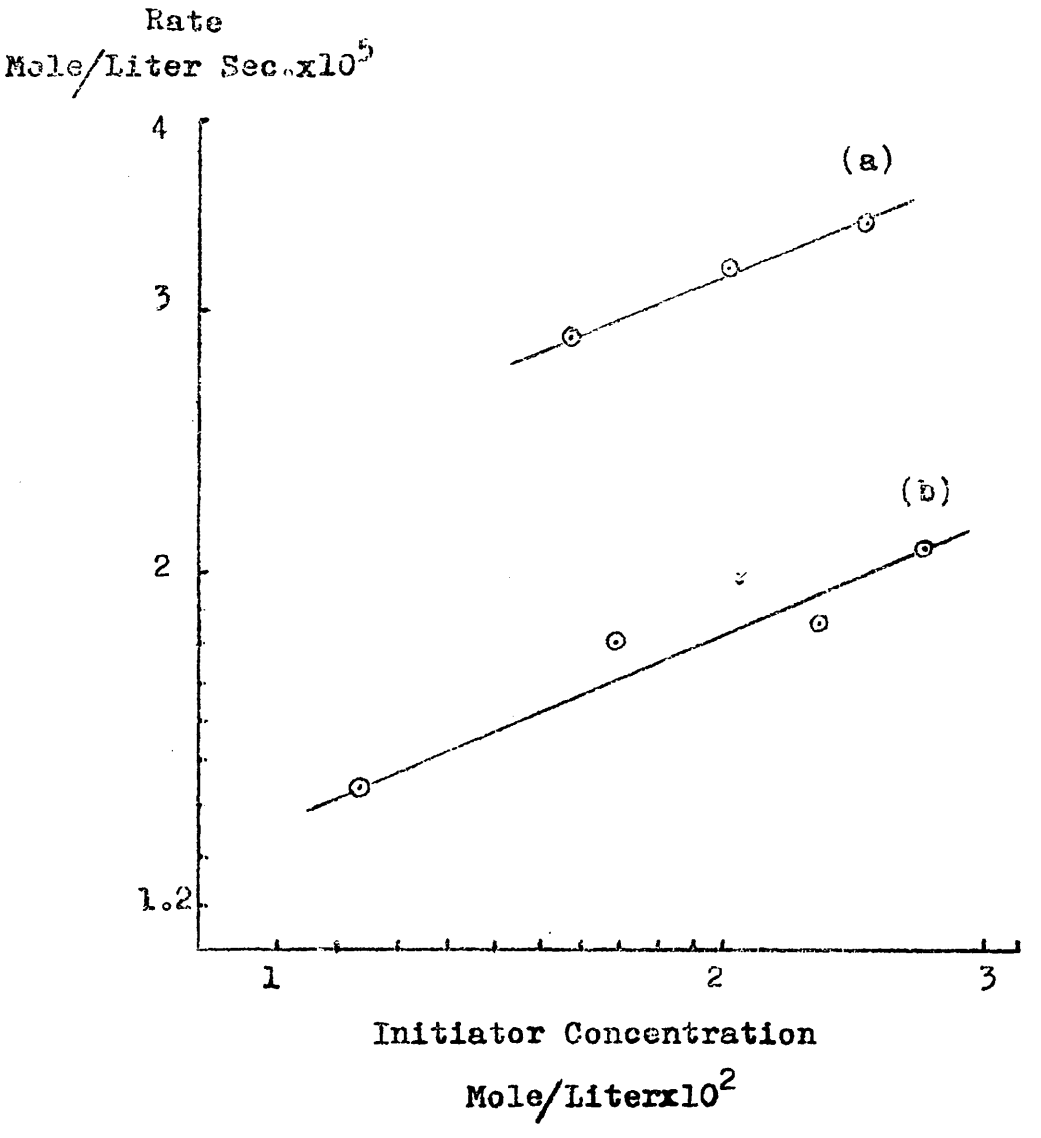
Monomer	Rate of Poly. mole/l.sec.x10^5	Ini. Conc. mole/l.x10^2	Exponent
4-Methyl-	2.89	1.58	
styrene	3.20	2.02	0.43
"	3.45	2.49	
2,4-Dimethyl-	1.44	1.14	
styrene	1.80	1.67	0.43
"	1.85	2.32	
"	2.08	2.73	

Table 9 (B)

Change of Polymerization Rate with Light Intensity.

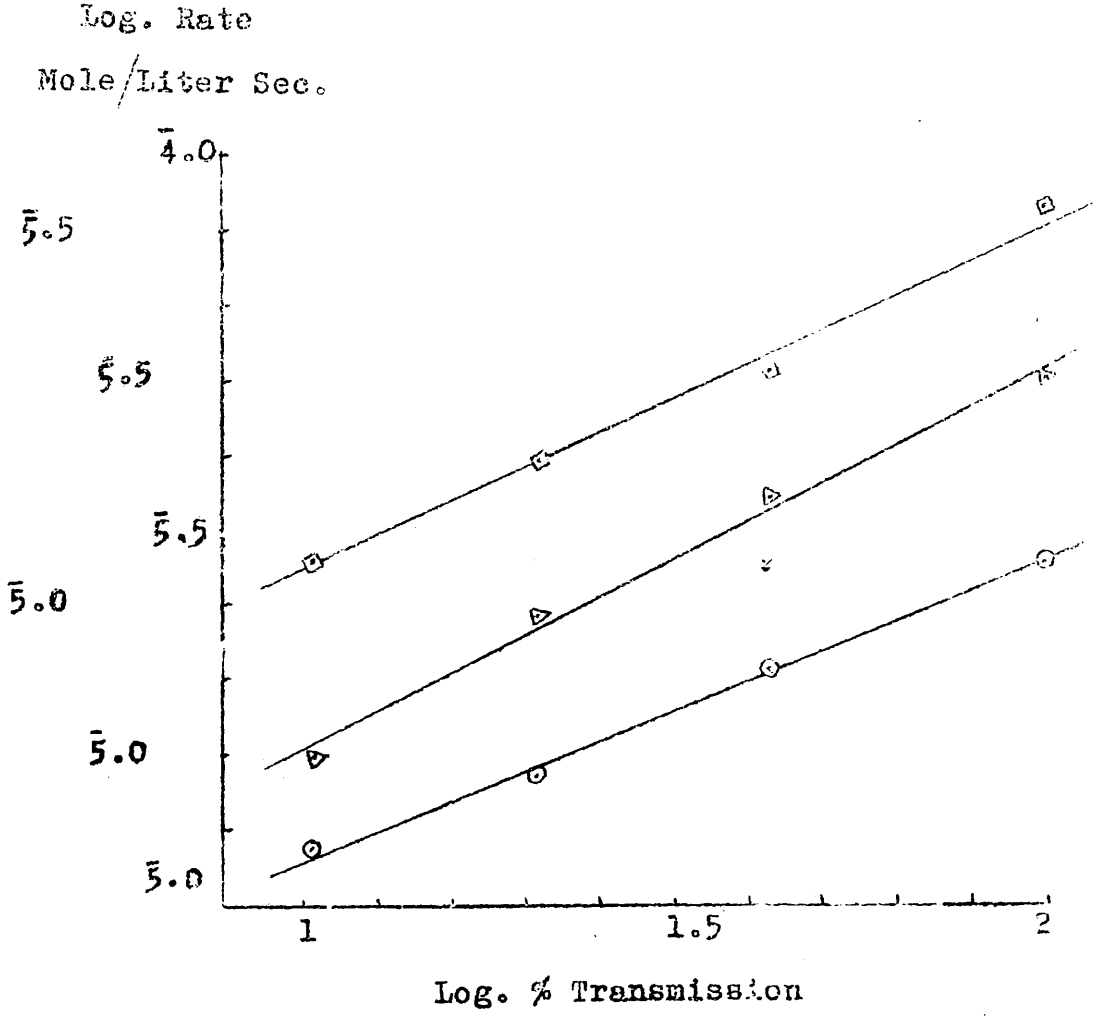
		% Transmission of Light.				
		10.4	20.9	42.6	100	
Monomer	Ini. Conc. mole/l x 10^2	Rate of Poly. mole/l. sec x 10^5				Expon.
4-Methyl	1.59	1.18	1.50	2.06	2.89	0.40
styrene	2.02	0.99	1.54	2.21	3.20	0.51
"	2.49	1.15	1.57	2.06	3.45	0.46
2,4-Dimethyl	1.14	0.58	0.84	1.06	1.44	0.40
styrene	1.69	0.75	0.99	1.42	1.80	0.42
"	2.32	0.82	1.02	1.41	1.85	0.38
"	2.73	0.94	1.25	1.59	2.09	0.38

Figure 15



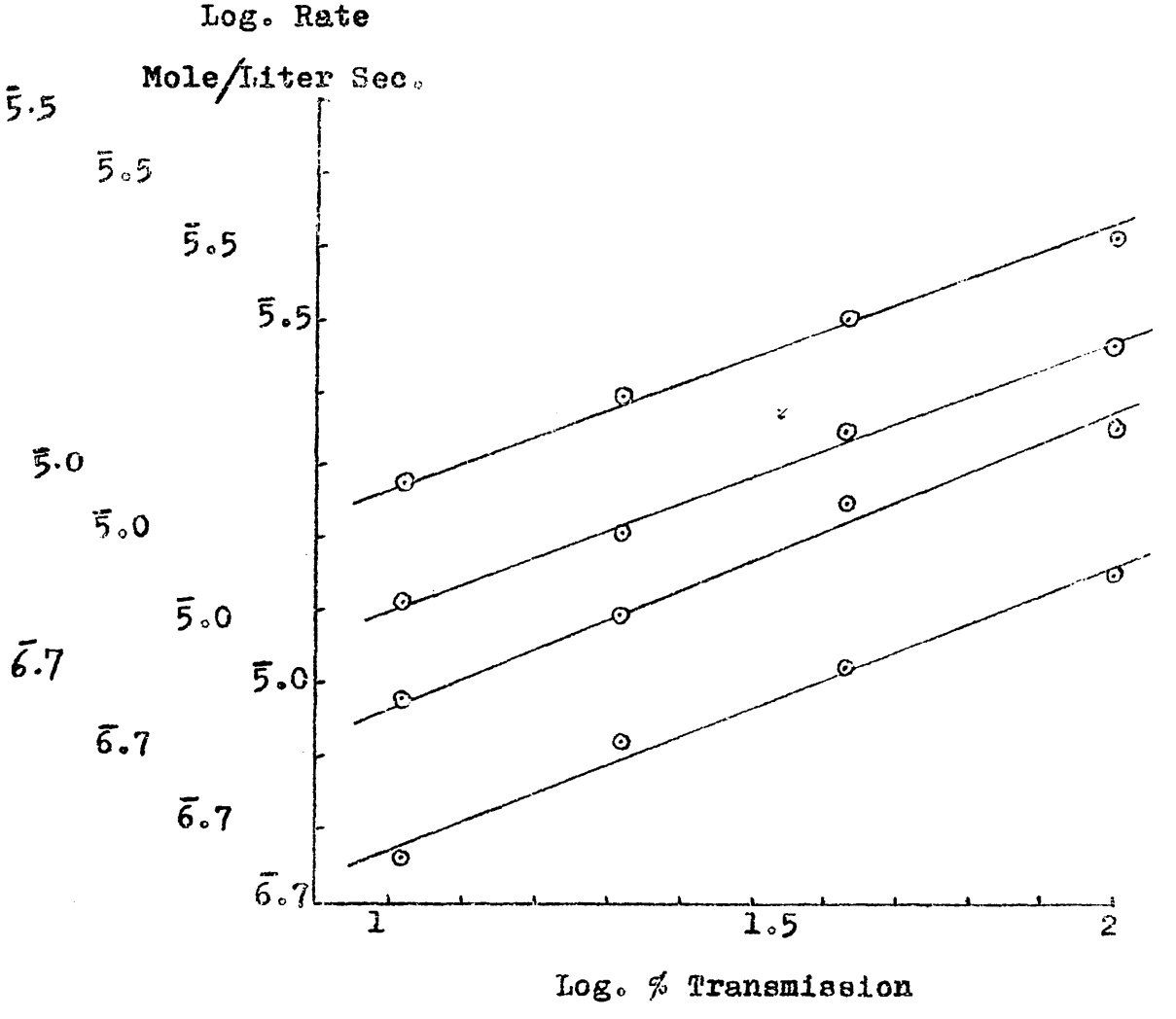
Logarithmic Plot Of Rate Of Polymerization Of 4-Methyl styrene (a) and 2,4-Dimethyl styrene (b) Against Initiator Concentration.

Figure 16 (A)



Logarithmic Plot Of Rate Of Polymerization Of 4-Methyl styrene Against % Transmission Of Light.

Figure 16 (B)



Logarithmic Plot Of Rate Of Polymerization Of 2,4-Dimethyl styrene Against % Transmission Of Light.

ii. Variation of Rate of Polymerization with Temperature:

The effect of temperature on the rate of polymerization of the above mentioned monomers, initiated by (AIBN) ~~are~~ is illustrated in Fig.17. and the results obtained summarized in Table 10.

In Fig.17. results for each monomer are compared at a fixed initiator concentration (0.0126 mole/l.)

On comparing the rates of polymerization at one fixed temperature, for example, 60°C , as shown in Fig.18 , one finds that the rate of polymerization decreases in the following order:-

styrene > 4-methyl styrene > 2,4-dimethyl styrene > 2,4,6-trimethyl styrene.

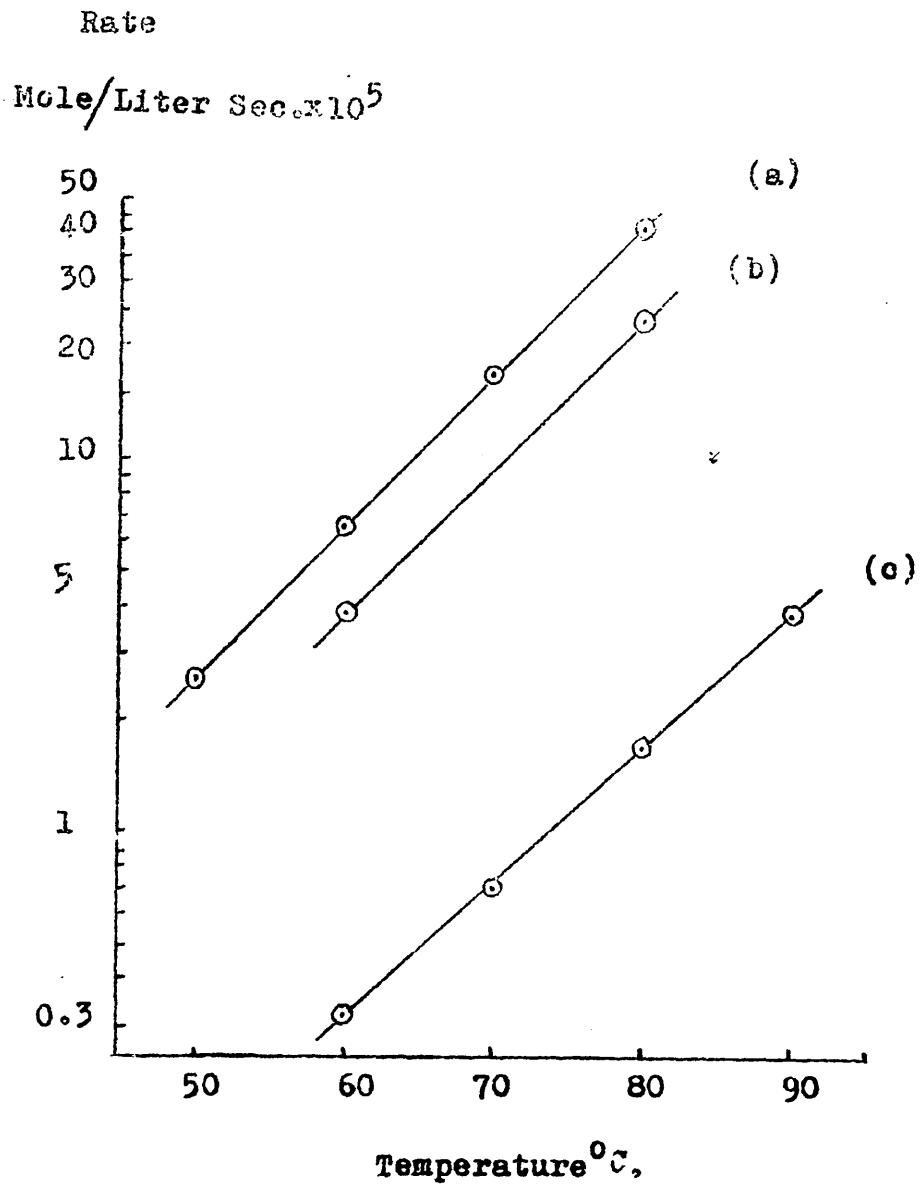
Therefore, it could be concluded, on the basis of these results, that the rate of polymerization, for each monomer, rises markedly with increase in temperature of polymerization. Moreover, the increase in number of methyl groups in the benzene nucleus, on passing from styrene to vinyl mesitylene, leads to a decrease in the rate of polymerization.

Table 10

Data for the Variation of Rate with Temperature at Constant Initiator Concentration.

Monomer	Temp. of Poly. t °C	Rate of Poly. mole/l. sec. x 10^5
4-Methyl	50	2.56
styrene (a)	60	6.58
"	70	16.87
"	80	41.69
2,4-Dimethyl	60	3.84
styrene (b)	80	23.60
2,4,6-Trimethyl	60	0.326
styrene (c)	70	0.706
"	80	1.71
"	90	3.85

Figure 17

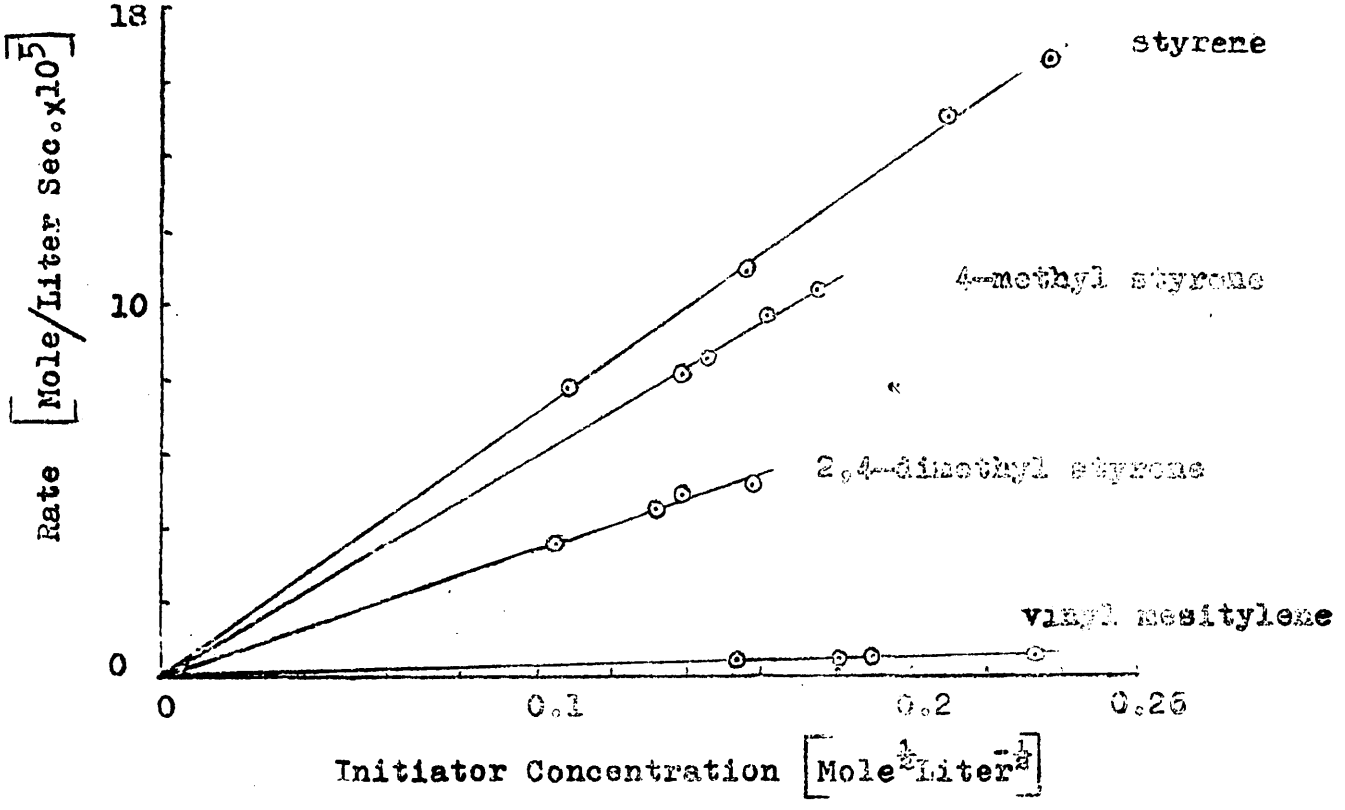


Variation Of Rate With Temperature At Constant Initiator Concentration.

Figure 18

Variation Of Rate With Initiator Concentration

At Constant Temperarure.



iii. Variation of Rate with Extent of Polymerization:

For each of the three monomers studied the rate of reaction was initially constant, but began to fall off gradually with time as the polymerization reaction proceeded. Similar effects have been reported in the literature with other monomers. For example, the decrease in the rate of styrene polymerization at about 10% conversion has been reported and commented on[60].

This could be explained in terms of the concentration of monomer and initiator decreasing, due to conversion of monomer to polymer and to the incorporation of initiator fragments into the polymer chains.

For this reason, in kinetic work, the initial rates are usually used. In practise, this is usually the average value over the first few per cent conversions (2-3%).

No attempts had been made to study the rate of polymerization at high conversions. It can be emphasized from Table 6. Chapter 2, that these experiments were all carried out to low conversions, usually below 10% , as at higher conversions cross linking, chain branching and other side effects may become significant.

iv. Variation of Molecular Weight with Initiator Concentration:

Molecular weights of the polymers studied over the temperature range 50 to 90°C , using various initiator concentrations (AIBN), are summarized in Table 6. of Chapter 2, where values of the molecular weights are listed as a function of the different initiator concentration.

It can be observed that at a fixed temperature, increase in initiator concentration decreases the molecular weight of the product polymer.

In the case of vinyl mesitylene, it can be deduced from the results obtained, that in this system, apparently, molecular weights are independent of the initiator concentration. Such a result may indicate that transfer reaction is important in the system.

Prat, Bengough and Norrish[61] and more recently Grant[62], have found similar effects in case of polyvinyl chloride and poly-α-chloro acrylonitrile respectively.

v. Determination of Rate Constants of Polymerization:

The prelimary results outlined above, with the exception of vinyl mesitylene, are in accord with the usual mechanism for free radical polymerization[63,64], which may be represented as follows:-

Initiation:	$C \xrightarrow{K_d} 2\dot{R}$	Rate $= f K_d(C)$
	$\dot{R} + M \xrightarrow{K_i} P_i^{\cdot}$	" $= K_i(\dot{R})(M)$
Propagation:	$P_r^{\cdot} + M \xrightarrow{K_p} P_{r+i}$	" $= K_p(\dot{P})(M)$
Transfer to monomer:	$P_r^{\cdot} + M \xrightarrow{K_f} M_r + P^{\cdot}$	" $= K_f(\dot{P})(M)$
Termination: Combination:	$P_r^{\cdot} + P_s^{\cdot} \xrightarrow{K_t} M_{r+s}$	" $= K_t(\dot{P})^2$
Disproportionation:	$P_r^{\cdot} + P_s^{\cdot} \xrightarrow{K_t} M_r + M_s$	" = "

Where, C = initiator $\dot{R}$ = initiator radical.

f = efficiency of initiator M = monomer unit.

K_d= velocity constant of the primary dissociation of initiator.

P_i, $P_r^{\cdot}$, and $P_s^{\cdot}$ = polymer radicals.

M_r, M_s and M_{r+s} = dead polymer molecules.

K_i, K_p, K_f and K_t = velocity constants of initiation, propagation, transfer and termination.

In case of photosensitized polymerization, the initiation step will be as follows:-

$$C + h\nu\ (E) \xrightarrow{K_d} 2\dot{R} \qquad \text{Rate} = f\,K_d(C)(I)$$

Where, E = energy of a quantum of light.

h = Plank's constant.

ν = frequency of light.

I = light intensity;

f = efficiency of both the incident light intensity and initiator concentrarion.

v.a. <u>The Steady State of Polymerization:</u>

This is known as the phase of the reaction in which the rate of formation and destruction of radicals, P, become constant in the early stages of the polymerization reaction, as follows:-

$$d[\dot{M}]/dt = -d[\dot{M}]/dt$$

$$\therefore \quad K_i(\dot{R})(M) = K_t(\dot{P})^2$$

The rate of the reaction is given by the rate of the propagation step, since it is the only one consuming up monomer in measurable amounts, hence :-

$$-d[M]/dt = K_p(\dot{P})(M)$$

$$R_p = K_p/K_t^{\frac{1}{2}}\ (M)\ (R_i)^{\frac{1}{2}}$$

$$\therefore \quad R_p = \text{constant} \times f\ (C)^{\frac{1}{2}}$$

$$\log.R_p = \tfrac{1}{2} \log.\ (C) + \text{constant.} \ . \ . \ . \ .$$

In case of photosensitized polymerization:

$$R_p = \text{constant} \times f\ (C)^{\frac{1}{2}}\ (I)^{\frac{1}{2}}$$

$$\log_e R_p = \tfrac{1}{2} \log_e (C) + \tfrac{1}{2} \log_e (I) + \text{constant}.$$

Thus, it can be observed that if termination is by the mutual interaction of two radicals, resulting either in combination or disproportionation, then in the early stages of the polymerization reaction, the rate of polymerization should be proportional to the square root of both the initiator concentration and the light intensity and to the first power of the monomer concentration.

The results obtained experimentally have previously been shown in Tables 8 and 9. and illustrated in Figs. 14, 15 and 16.

b. Determination of $K_p/K_t^{\frac{1}{2}}$ and K_f/K_p by the Molecular Weight method:

Since the average molecular chain length or degree of polymerization is defined as:-

$$\frac{\text{Rate of Consumption of Monomer}}{\text{Rate of Termination of Chains}}$$

that is to say:-

$$C.L = \overline{D.P} = \frac{R_p}{R_t + R_f} = \frac{K_p(P)(M)}{K_t(P)^2 + K_f(P)(M)}$$

$$\therefore \quad \frac{1}{C.L} = \frac{1}{\overline{D.P}} = \frac{K_f}{K_p} + \frac{K_t}{K_p^2\ M^2} R_p$$

Therefore, the plot of $1/C.L$ as a function of the measured rate of polymerization, is a straight line, with the intercept K_f/K_p on the $1/C.L$ axis and the slope of which will give the value of $K_t/K_p^2 M^2$.

The values of $K_p/K_t^{\frac{1}{2}}$ and K_f/K_p calculated from the slopes and intercepts respectively, from Fig. 19, are quoted in Table 11.

Table 11

Data for the Rate Constants Ratios

Monomer	Temp. of Poly. t^oC	$K_f/K_p \times 10^5$	$K_p/K_t^{\frac{1}{2}} \times 10^2$
4-Methyl	50	5.4	3.05
styrene.	60	8.4	4.36
"	70	11.6	6.00
"	80.	15.8	9.32
2,4-Dimethyl	60	13	3.04
styrene.	80	24	5.31
2,4,6-Trimethyl	60	250	0.723
styrene.	70	350	1.14
"	80	400	1.71
"	90	500	2.07

Figure 19 (a)

Determination Of K_f/K_p And $K_p/K_t^{\frac{1}{2}}$ For 4-Methyl styrene.

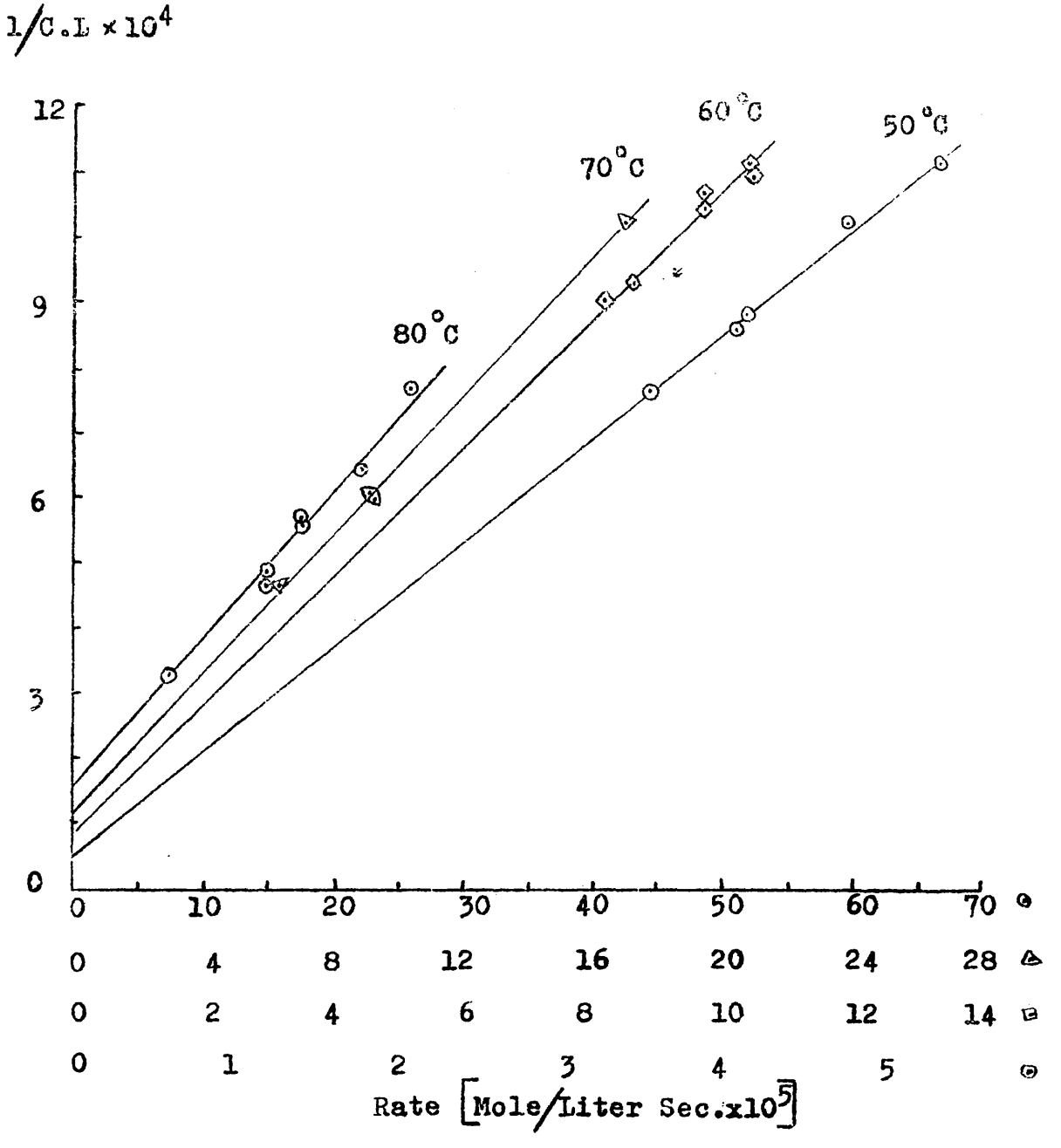
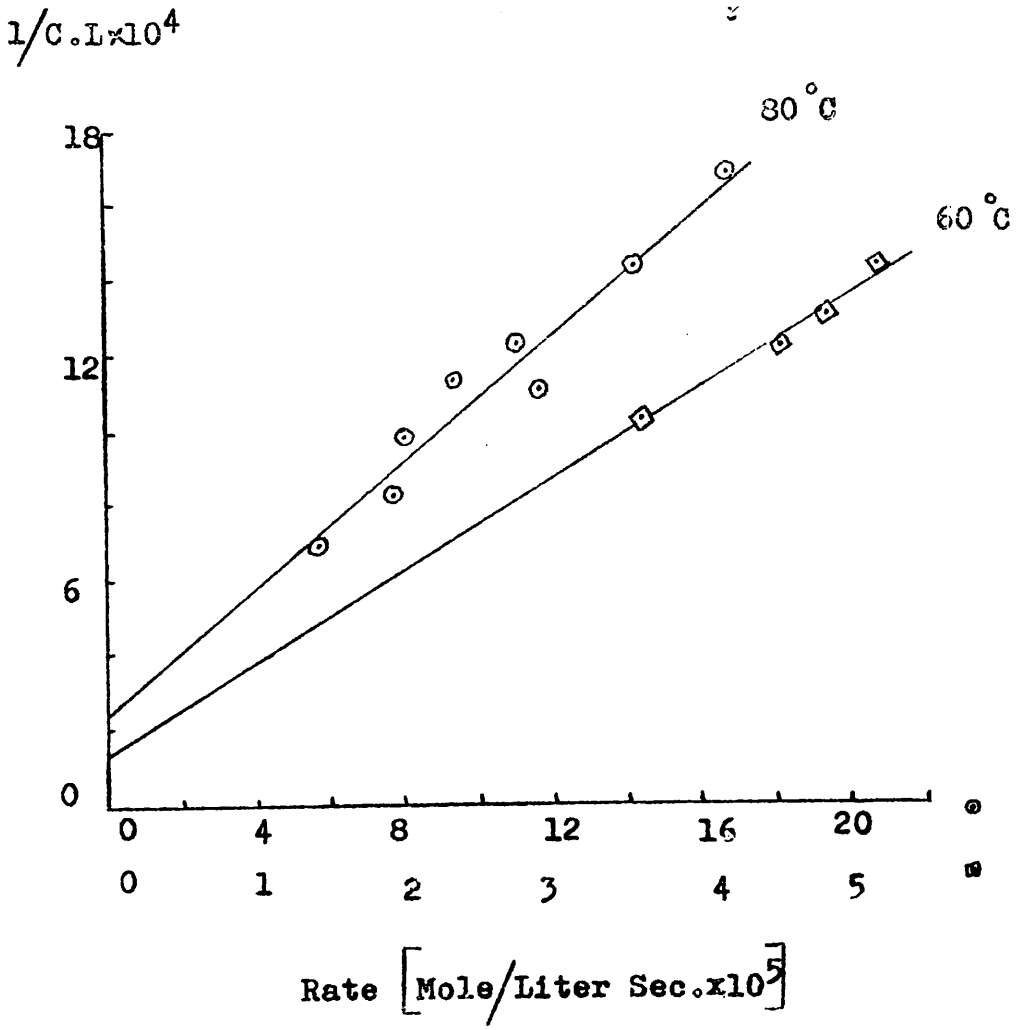


Figure 19 (b)

Determination Of K_f/K_p And $K_p/K_t^{\frac{1}{2}}$ For 2,4-Dimethyl styrene.



c. Determination of the Activation Energies:

Using the data in Table 10 and applying the Arhenius relationship, overall energies of activation can be obtained from the log. rate versus 1/T A (absolute temperature) plot as in Fig.20. Results are quoted in Table 12.

From the kinetic scheme and the assumption of the steady state, the rate of polymerization can be shown to be given by:-

$$R_p = K_p M R_i^{\frac{1}{2}} / K_t^{\frac{1}{2}}$$

Hence, the overall energy of activation is that of the term $K_p K_i^{\frac{1}{2}} / K_t^{\frac{1}{2}}$, consequently the overall energy of activation could be expressed as the following:-

$$E_o = E_p + \tfrac{1}{2} E_i - \tfrac{1}{2} E_t .$$

Where, E_o, E_i, E_p and E_t are the overall activation energy and the activation energies of initiation, propagation and termination respectively. In the catalysed polymerization, E_i refers to the decomposition of the initiator into radicals.

From the data given in Table 11 the activation energies of K_f/K_p and $K_p/K_t^{\frac{1}{2}}$ terms are calculated. These are illustrated in Figs.21 and 22. and the corresponding values obtained are shown in Table 12.

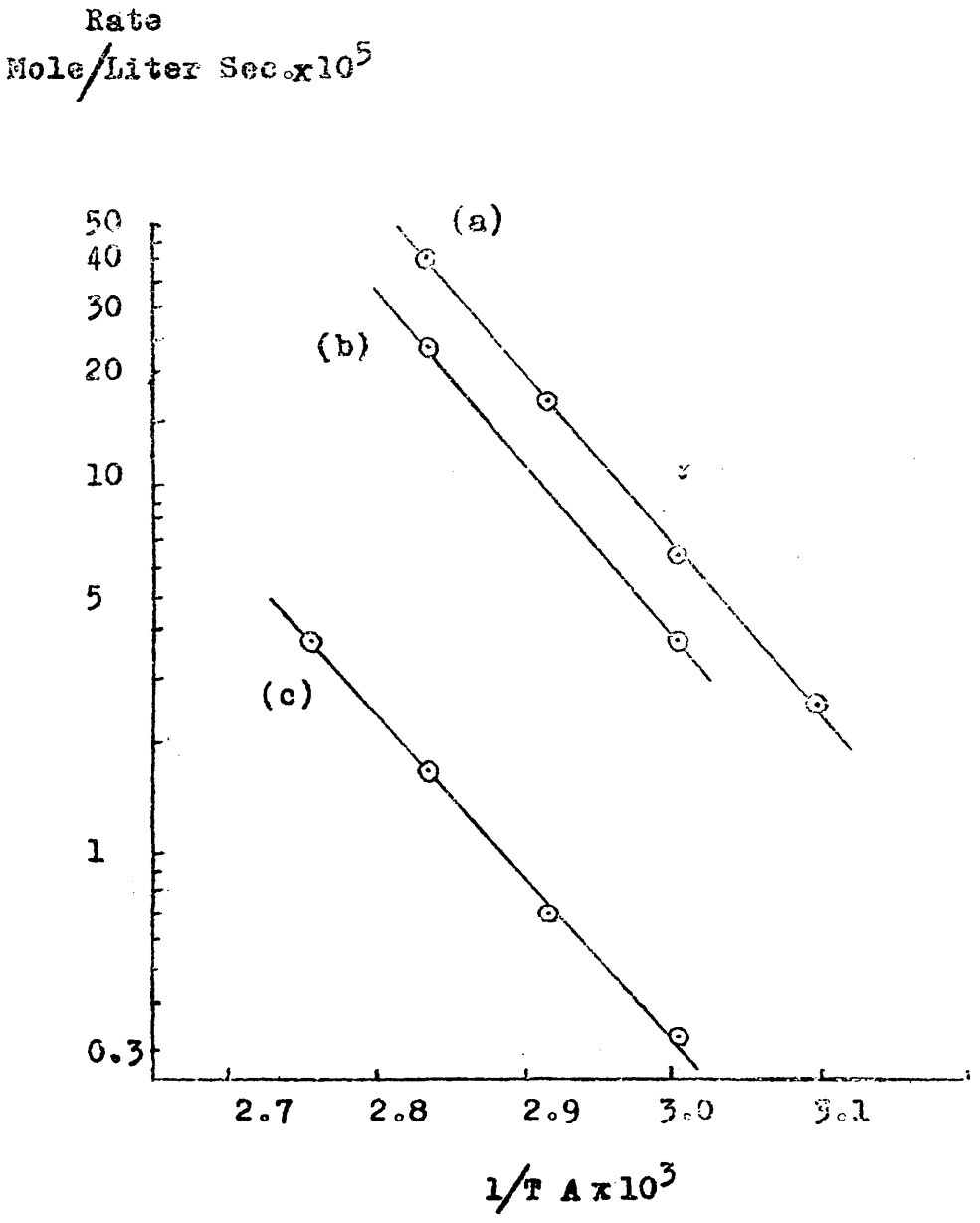
Table 12

Data for the Activation Energies (k.cal./mole)

Monomer	E_o	$E_f - E_p$	$E_p - \frac{1}{2} E_t$
4-Methyl styrene (a)	21.0	7.9	8.7
2,4-Dimethyl " (b)	21.1	7.1	7.6
2,4,6-Trimethyl " (c)	19.9	5.0	9.0

It can be observed from the data in Table 11 that there is an increase in the values of the ratio K_f/K_p and a decrease in the values of $K_p/K_t^{\frac{1}{2}}$, with increase of number of methyl groups in the monomer. Consequently, the data given in Table 12 shows that there is a reduction in the activation energy of the $(E_f - E_p)$ term and an increase in the value of the $(E_p - \frac{1}{2}E_t)$ term, with the exception of 2,4-dimethyl styrene.

Figure 20



Overall Activation Energies.

Figure 21

Activation Energies Of K_f/K_p .

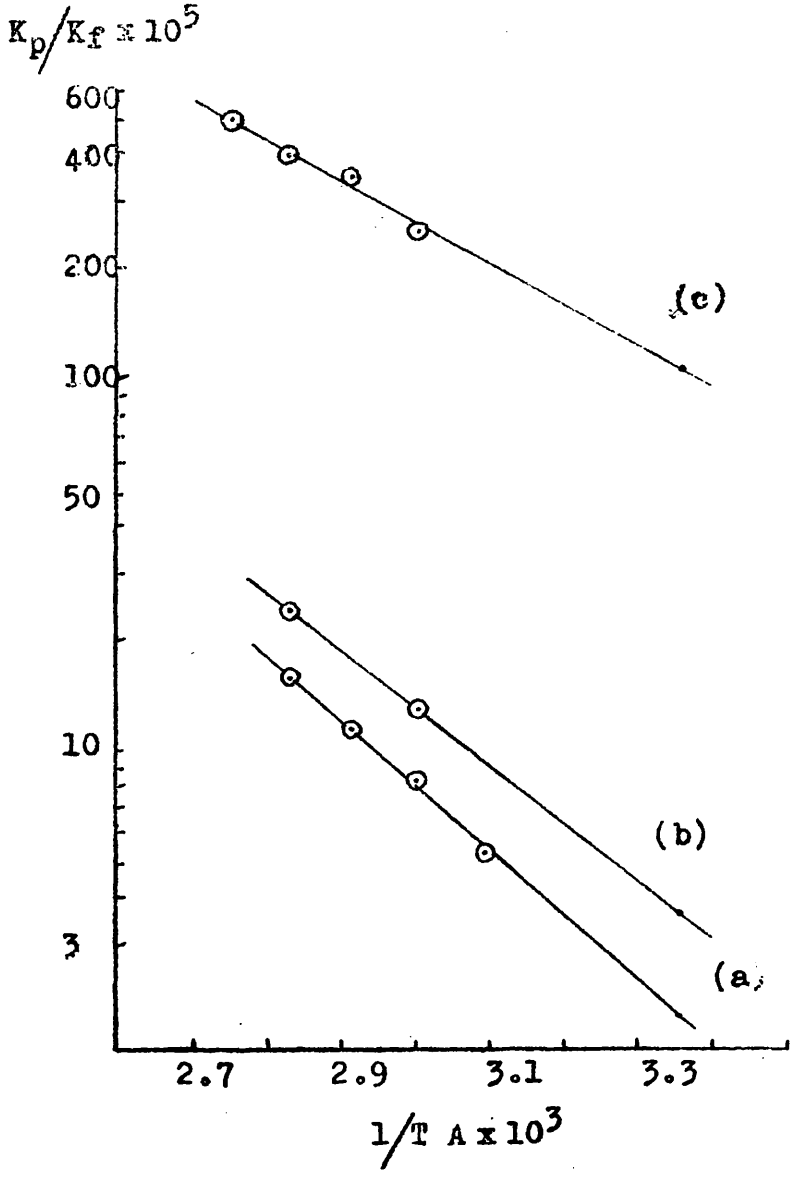
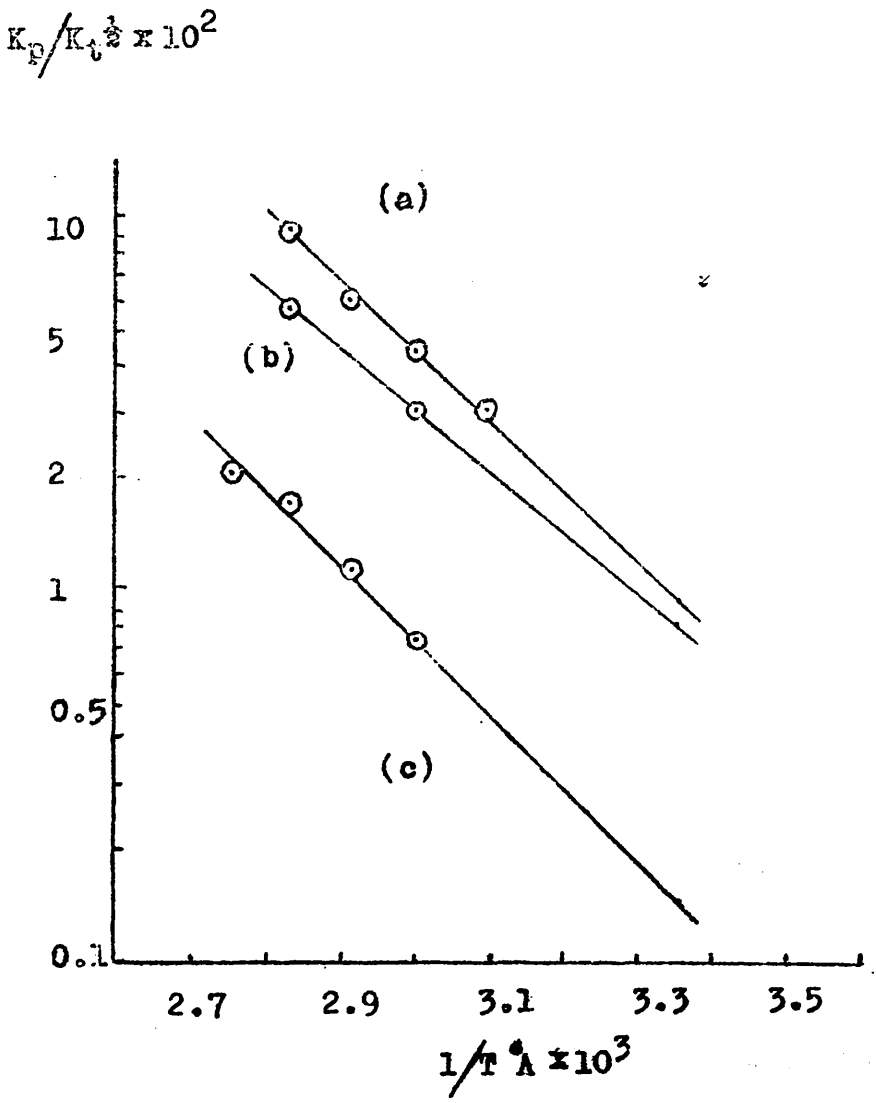


Figure 22

Activation Energies Of $K_p/K_t^{\frac{1}{2}}$



[illegible]

In order to obtain individual [illegible] constants K_p, K_t and K_d, it is necessary to obtain some relationship between them. This may be obtained by measuring the lifetime of the growing radicals, which is defined by :-

$$\tau = \frac{\text{Concentration of active centres}}{\text{Rate of disappearance of active centres}}$$

$$\therefore \quad \tau = P/K_t(P)^2 = 1/K_t(P)$$

Consequently it can be shown that:-

$$K_p/K_t = \tau R_p/M.$$

The lifetime of the growing radical is measured by applying the method of intermittent illumination, with Burnett and Melville[52] theoretical treatment, using the rotating sector technique, described in Chapter 2.

The rate of the reaction will be proportional to the concentration of the propagating radicals, so, the ratio of the radical concentration $(P_s)/(P_o)$ may be replaced by the ratio of the measured rate $(R_s)/(R_o)$.

Where, P_s & R_s = concentration of radicals and rate of polymerization respectively, under intermittent illumination.

P_c & R_o = concentration of radicals and rate of polymerization under full illumination.

Hence the rate of polymerization was measured under full illumination and intermittent illumination and the ratio $(R_s)/(R_o)$ was evaluated.

The value of the lifetime of the active polymer radical may be determined in two ways:-

When the rate of the reaction is plotted against log. flash time, a curve of the type shown in Fig.23 is obtained. At the period when the flash time approximates to the lifetime of the radical, a change of rate will occur. From this change the approximate value of the lifetime can be obtained.

By fitting the experimental ratio of $(R_s)/(R_o)$ to the theoretical curve constructed from values quoted in reference (52) by Burnett and Melville, results were obtained as shown in Fig.24. Where m is the number of times the flash time t is greater than the lifetime τ, therefore, $\tau = \frac{t}{m}$.

Thus it is necessary to know the rate at some intermediate speeds of rotation and the rate at fast rotation.

Consequently, the individual rate constants of the polymerization reaction can be determined, since from molecular weight measurements the value of $K_p/K_t^{\frac{1}{2}}$ can be determined and from the rotating sector experiments we obtain the value of K_p/K_t.

The values of the separate rate constants for

the polymerization of 4-methyl styrene and 2,4-dimethyl styrene at 25°C. along with those obtained by other investigators, are shown in Table 13.

Table 13

Individual Values for the Rate Constants (l./mole sec.)

Monomer	Temp. t°C.	K_p	$K_t \times 10^{-7}$	$K_f \times 10^{3}$	E_o	τ sec.	Ref.
Styrene.	30	106	10.8	-	21.3	1.20	65
"	40.5	120.5	-	-	-	-	66
4-Methyl	25	64.7	4.8	1.32	21.0	2.25	*
styrene.	30	84	6.6	-	22.1	2.10	65
"	40.2	102.7	-	-	-	-	66
2,4-Dimethyl	25	40.0	2.37	1.49	21.1	2.75	*
styrene.							

The data in the above Table (13) shows that there is a reduction in the value of the propagation rate constant and an increase in the value of the lifetime of the growing radical, on passing from styrene to 2,4-dimethyl styrene.

* present work.

Determination Of The Value Of τ For 4-Methyl styrene

Figure 24 (a)

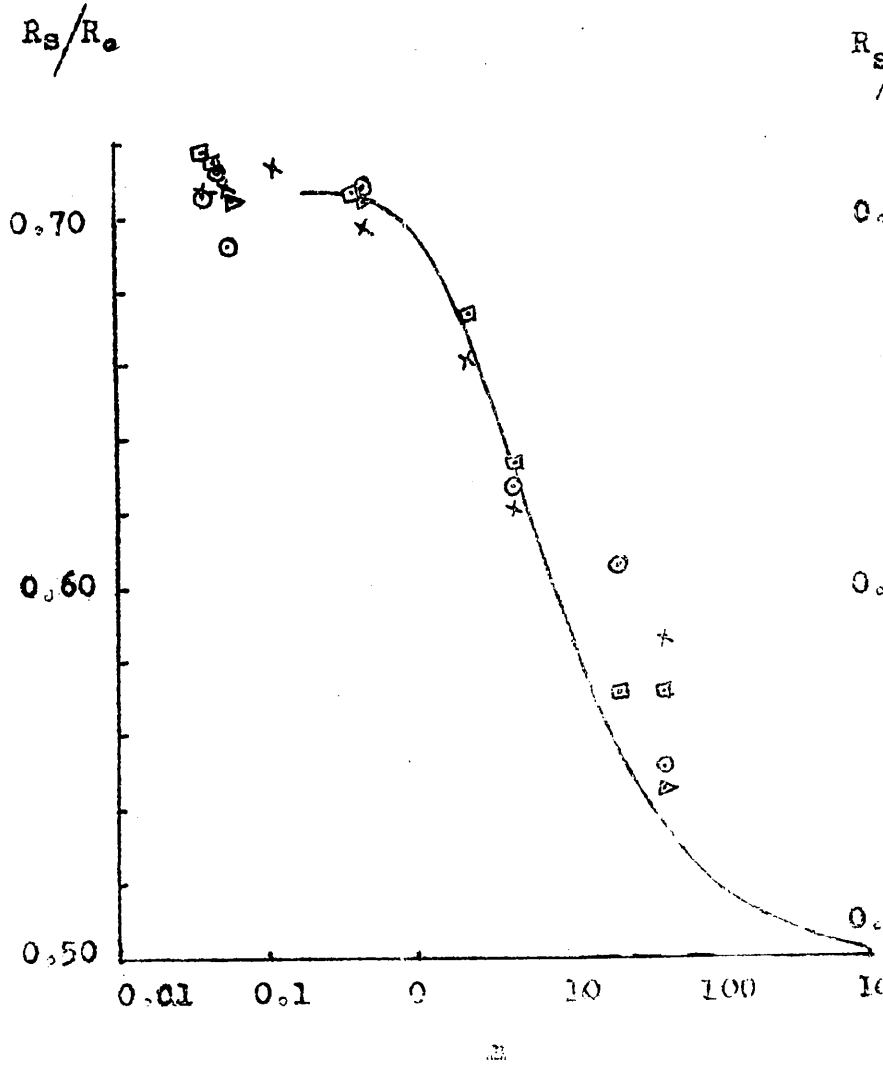
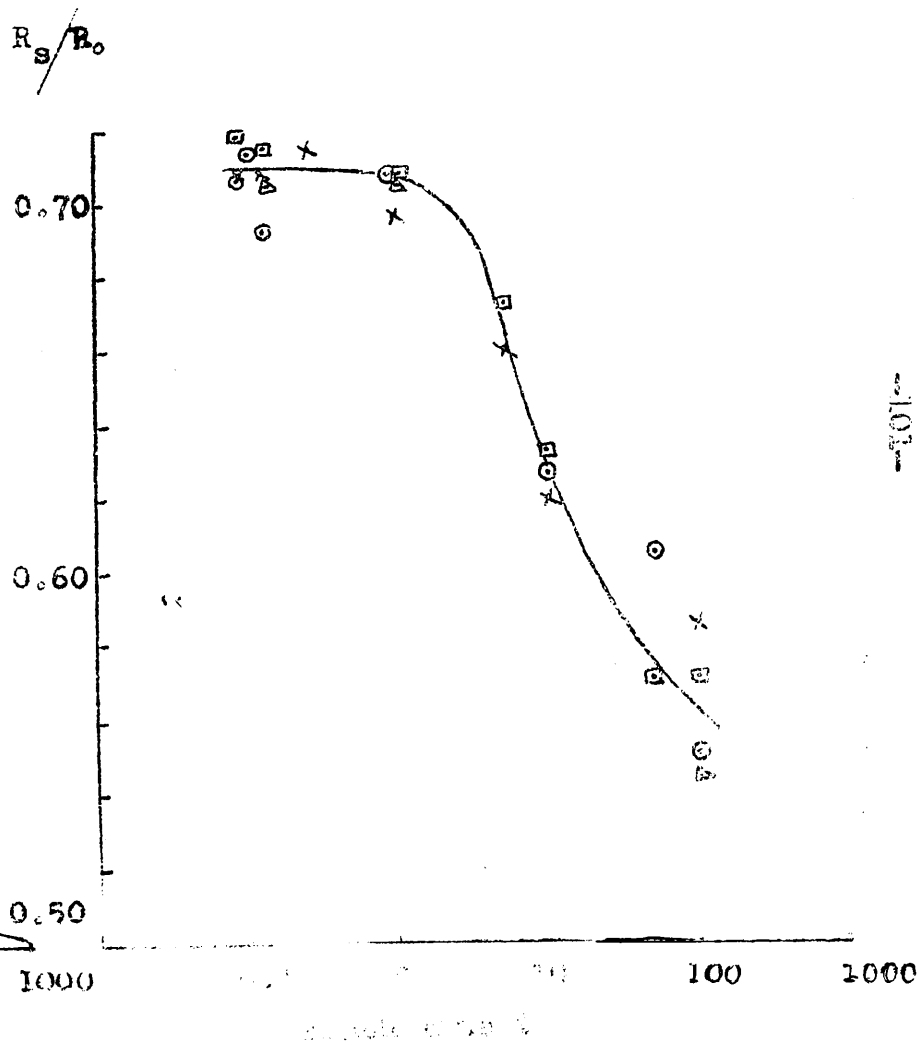


Figure 23 (a)



Determination Of The Value Of γ For 2,4-Dimethyl styrene.

Figure 24 (b)

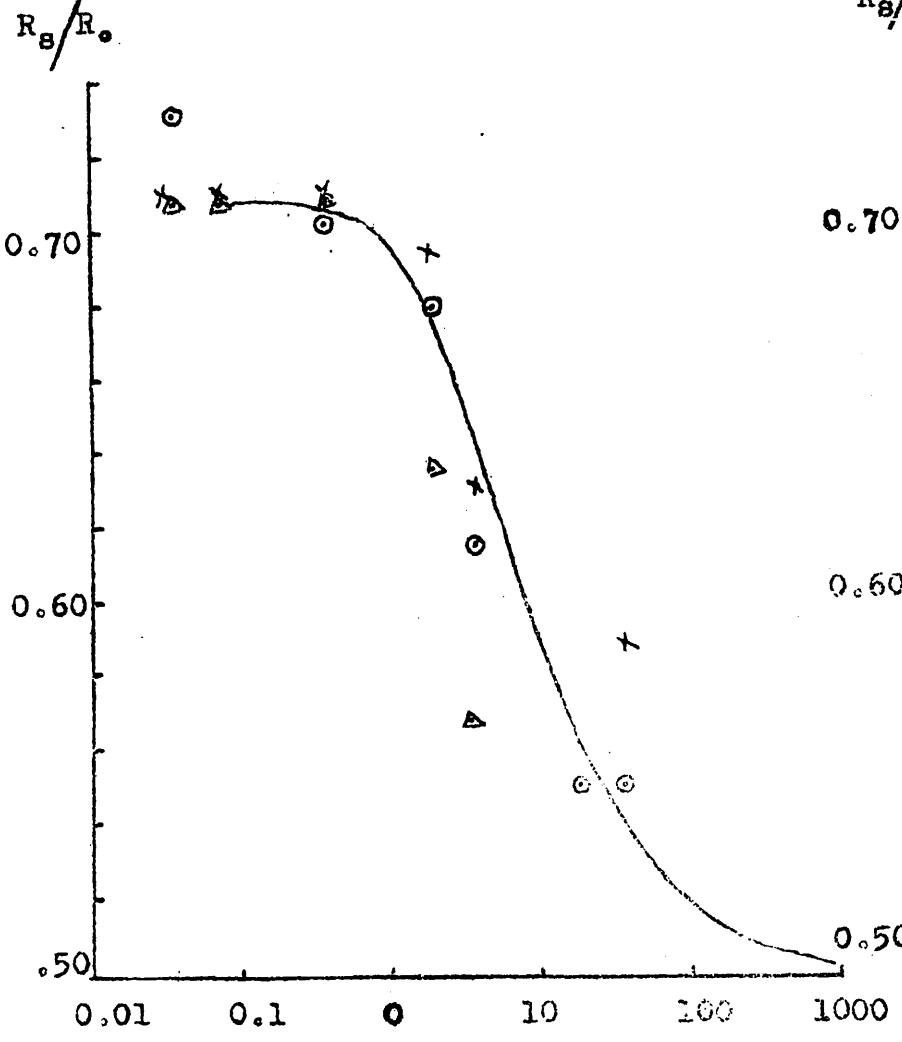
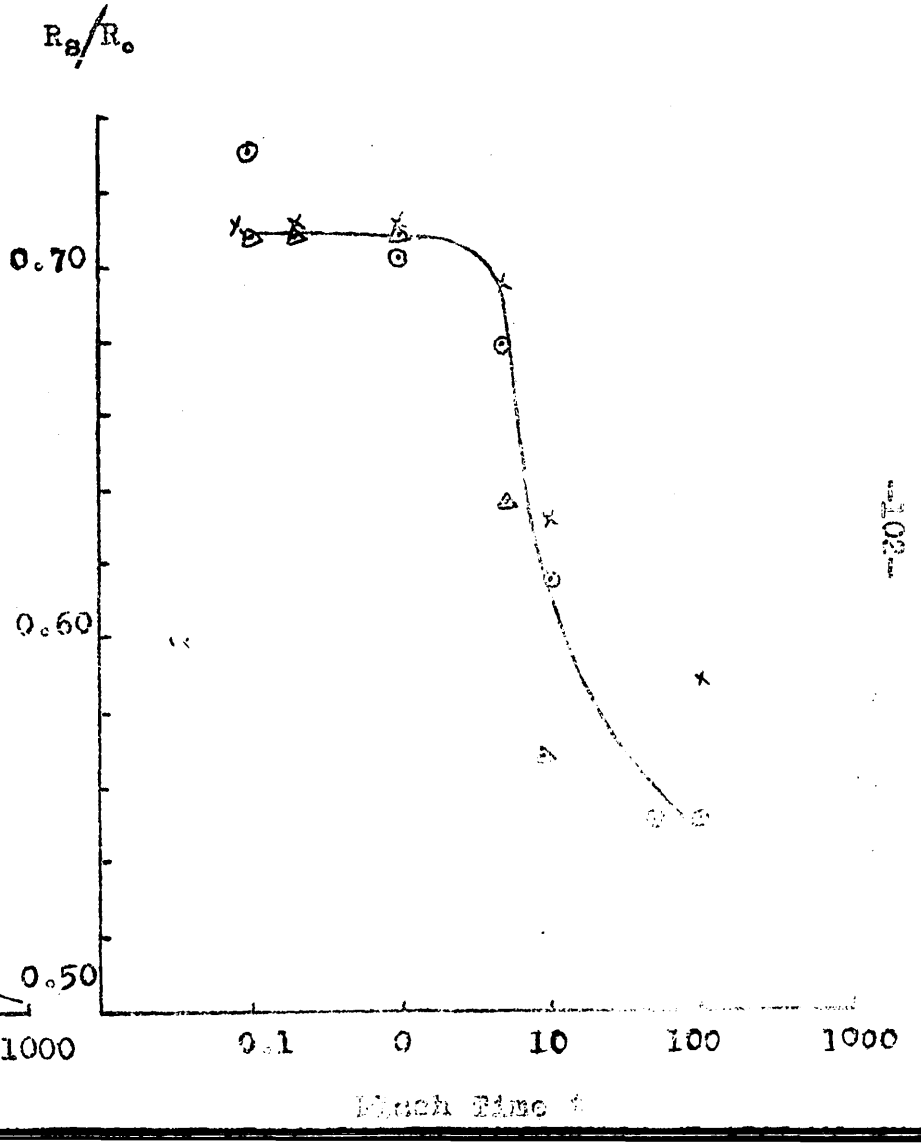


Figure 23 (b)



Kennedy and Brownlee[60] studied the [illegible] polymerization of p-methyl styrene, 2-methyl styrene, 2,4,5-trimethyl styrene and 2,4,6-trimethyl styrene. They found that nuclear methylation in the benzene ring of styrene have a marked effect in reducing the volume contraction and the coefficient of expansion of the monomers compared with styrene. A similar effect has been observed in the present work (See Table 2 and 3 Chapter 3). These observations were explained in molecular terms, being connected with the reduced ability of the monomer and polymer molecules to pack together.

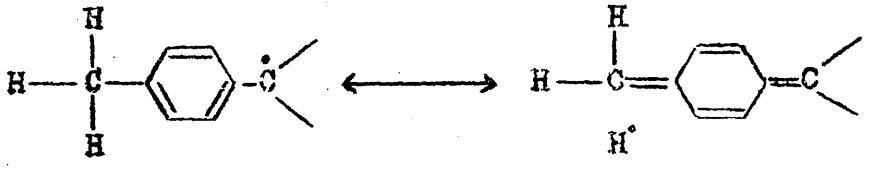
Also the overall activation energy of polymerization appears to be some what reduced by nuclear methylation.

Moreover, they found that 2,4,6-trimethyl styrene polymerizes with great difficulty; the same observation has been found in the present investigation.

They came to the conclusion that the major effect of such substitution may be attributed to a change in the resonance stability and the reactivity of the free radicals. The presence of two ortho methyl groups have a profound effect on the nature of styrene due to steric effects and that one ortho methyl group has a much smaller effect.

Recently Paoletti and Billmeyer[66] determined the absolute rate constants for the emulsion polymerization of styrene, o-methyl styrene, p-methyl styrene and vinyl toluene.

They found that the rate constants for propagation are lower for substituted monomers than for styrene. The differences are attributed to increased radical stability from methyl group contributions to resonance structures and to steric hindrance of the ortho methyl group. They applied the assumption made by Gould[69] that the unpaired electron of the newly formed radical is delocalized by hyperconjugation as follows:-



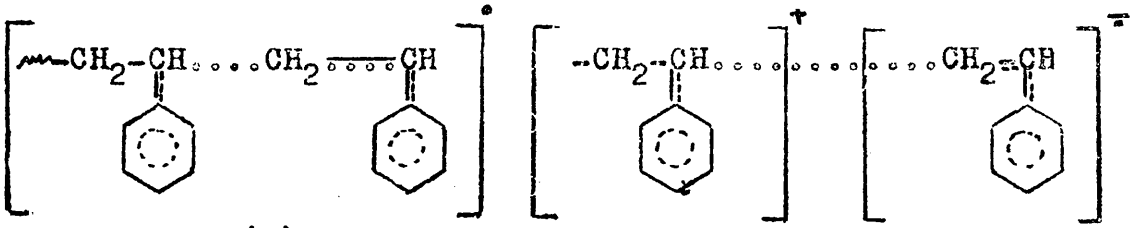
Some of their results are shown in Table 13.

More recently Imoto, Kinoshita and Nishigaki[65] studied the free radical polymerization of styrene and p-substituted styrenes, among which is p-methyl styrene, and determined the individual rate constants. This are quoted in Table 13.

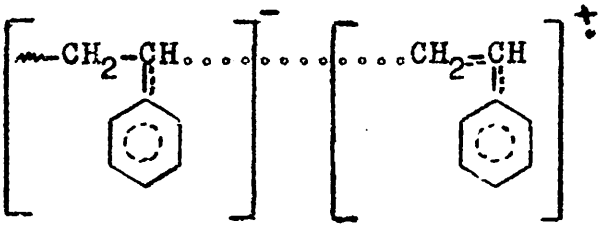
From their results, it can be observed that the rate of polymerization of p-methyl styrene is lower than that of styrene, and consequently a reduction in the

propagation rate constant. Moreover there is an increase in the overall activation energy, the activation energy of the propagation step and the lifetime of the growing polymer radical.

They assumed that there is a participation of ionic structures in the transition state of the propagation reaction as follows:-



(I)



(II)

Where structure I corresponds to resonance interaction and II to the polar effect. They found that the styrenes with more electron-attracting substituents show a greater overall rate of polymerization . They suggested that the ease of propagation may increase with the contribution of polar structures which participate with resonance structures.

C. Discussion and Conclusion:

1. Monomer and Radical Reactivity:

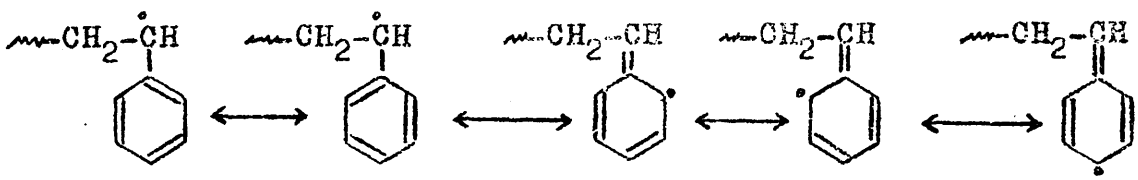
The reactivity of unsaturated monomers with free radicals depends on the structure of both the olefin and the radical.[64] The reactivity of any substituted ethylene towards a free radical depends on the substituent group; usually a second substituent on the same carbon atom increases the reactivity. Methyl methacrylate, for example, is more reactive than methylacrylate. Olefins with substituent groups which stabilize the product radical are also stable monomers, but the stabilization of the monomer is small in comparison to the stabilization of the radical. Thus the overall effect is a greater reactivity, where a radical, which is stabilized through delocalization can be formed.

Resonance stabilization, on the other hand, depresses the reactivity of the radical towards a monomer. The effect of a substituent on the radical, however, is much greater for depressing its reactivity than enhancing the activity of the monomer.

As mentioned earlier in this Chapter, it has been suggested that the polystyryl radical occasionally reacts in one of its alternative canonical forms with the radical center on the benzene ring. Thus in the present work, we have to consider the effect of methyl substituents in the

styrene ring, on the rate of normal polymerization (head to tail addition through the vinyl group) and on the extent of abnormal polymerization (radical addition to the ring). The rate of normal polymerization will be determined by the extent to which the substituents stabilize or destabilize the monomer and the radical derived from it. The extent of abnormal polymerization will depend on the activation by the substituents of the positions in the ring and upon the steric effects of the substituents.

For the styrene radical the following resonance structures can be written:-



With the result that the ortho and para positions are activated for free radical addition polymerization. No further stabilization of methyl substituted styrenes would be expected from this effect (conjugative effect).

When methyl groups are introduced into the benzene ring of styrene, at the ortho and para positions, further stabilization becomes possible by means of hyperconjugation. Gould[69] suggested that substitution at the ortho and para positions may delocalize the unpaired electrons by hyperconjugation as follows:-

Thus stabilization by hyperconjugation should increase with an increasing number of methyl groups in the radical as follows:-

styrene < 4-methyl styrene < 2,4-dimethyl styrene < 2,4,6-trimethyl styrene.

I II III IV

This increase in the stability of the monomer and its radical will lead to a reduction in the rate of polymerization. This is consistent with the experimentally observed order of reactivities:-

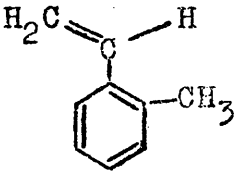
IV < III < II < I

Accordingly, there is a reduction in the value of the propagation rate constant and an increase in the lifetime of the growing polymer radical, relative to styrene, as can be deduced from Table 13, with the increase of the number of methyl groups in the monomer.

The introduction of methyl groups in the ortho positions of styrene will produce steric interaction[70] with the vinyl group. This interaction will be at a minimum when the planes of the ring and the vinyl group are perpendicular to each other. Resonance stabilization however, requires the vinyl group and the benzene nucleus

to be coplanar and this will be expected under these conditions. Thus ortho methyl groups would be expected to reduce the resonance stabilization because of steric repulsion, but meta or para substituents would not have this effect.

In the presence of one methyl group in an ortho position, coplanarity may still be achieved if the vinyl group is rotated away from the ortho methyl group as follows:-



But with a second ortho methyl group this would not be possible. Ortho substituents might ,also hinder the approach of a monomer unit for reaction.

As a result of the steric effect of ortho methyl groups the stability of the radicals will decrease. This will be accompanied by an increase in the activation energy,as additional energy is required to force the radical to its transition state. This in turn, together with the probability of steric interference with the approaching monomer units, will lead to a reduction in the rate of the reaction.

Vinyl mesitylene monomer is found to polymerize with great difficulty and the rate of polymerization is very low. Moreover, the molecular weights are low and

and independent of the initiator concentration at first, there is a probability that degradative transfer might be important in this system, and also termination of the polymer radicals by the small initiator radicals might take place. The initiator exponent is found to be less than 0.5, which indicates that termination by primary radicals might take place to some extent. These experimental findings can be explained satisfactorilly on the basis previously mentioned.

Therefore, the results of the polymerization of vinyl mesitylene, in the present work, are not so reliable.

CHAPTER 4

THERMAL DEGRADATION OF POLYSTYRENE PREPARED BY FREE RADICAL MECHANISMS

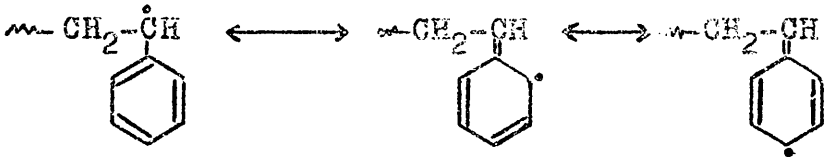
A. Introduction:

It is clear from the material presented in Chapter 1 that detailed investigations so far have been limited to the thermal degradation of polystyrene prepared by free radical mechanisms. It has previously been pointed out that the rapid fall in molecular weight during the initial stages of the reaction has been associated with chain scissions at weak links which are regarded as being distributed at random along the polymer chains.

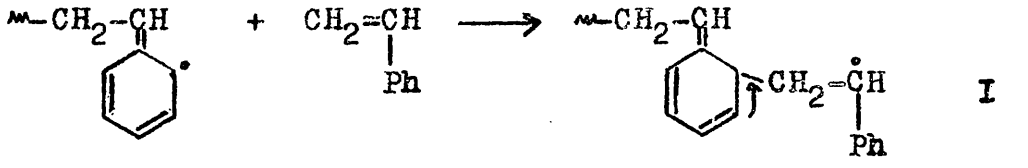
Grassie and Kerr[29] suggested, on the basis of their results, that labile structural abnormalities are produced during the polymerization process by some abnormal reaction which occurs in direct competition with the normal polymerization propagation step, which is head to tail addition of monomer units, but has a slightly higher energy of activation.

Later, Grassie and Cameron[30] concluded from their results that this abnormal process is not head to head addition, and since the stability of the polystyryl radical is attributed to resonance structures with the radical centre in the benzene ring, they suggested the

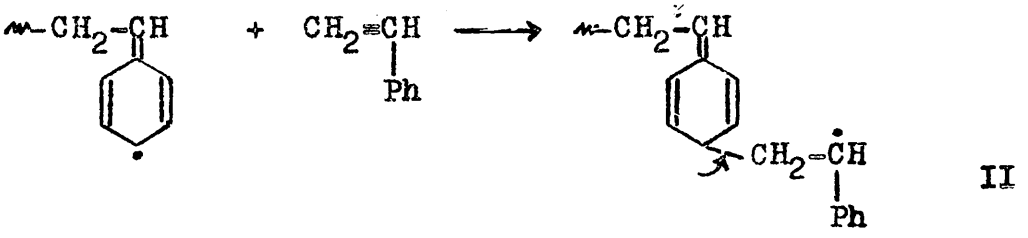
possibility of polymerization through an alternative canonical form of the growing polymer radical:-



These forms should be capable of adding monomer units, giving rise to structures of the following types:-



I



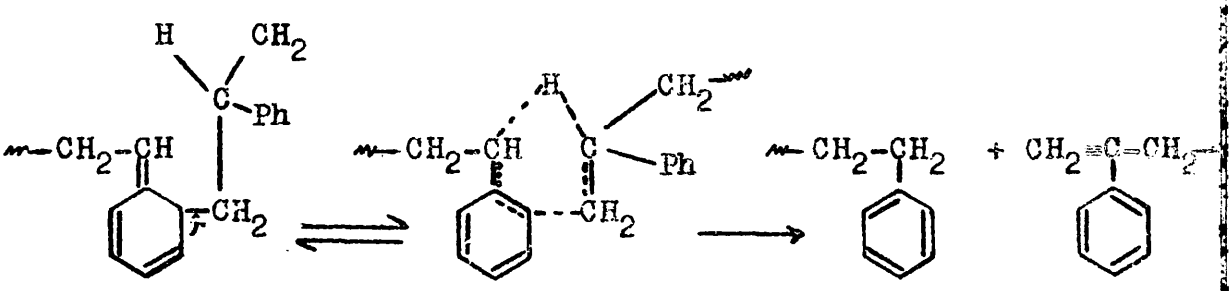
II

The C-C bonds indicated in structures I and II would be expected to be more thermo-labile than the normal C-C bonds in the polymer backbone, being next but one to two double bonds.[36]

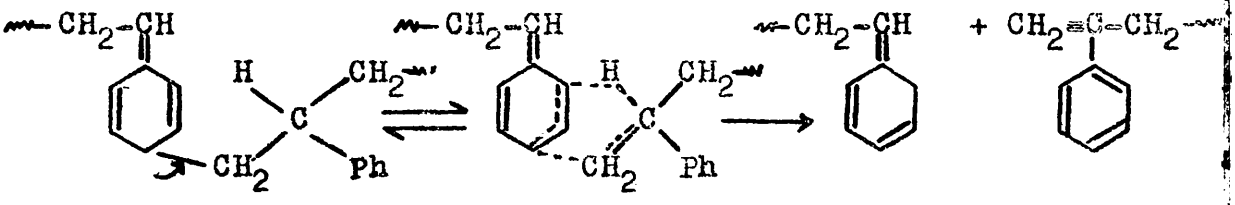
Ozonization of polystyrene[31] has shown that it contains backbone double bonds in the same concentration as thermo-labile links. The conclusion drawn from these results is that weak links in polystyrene are associated with unsaturation in the main polymer chain. These authors proposed the following scheme, which assumes that weak links are quinonoid structures and that free radicals

do not appear at any stage of their breakdown:-

Ortho type Weak Link:



Para type Weak Link:



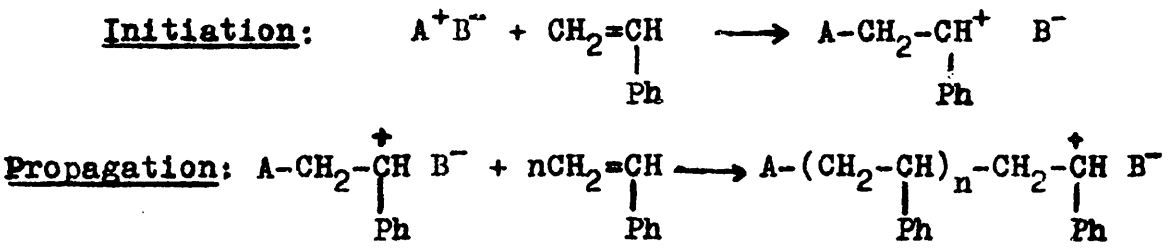
transition state

However, any weak link theory must account for the degradation behaviour of ionically prepared polystyrenes, since these also appear to contain structural abnormalities which act as weak links. In this case of course it is to be expected that the type, or at least the concentration of weak bonds would be different from that in radical initiated reactions. Thus it seemed important to make a brief study of the thermal

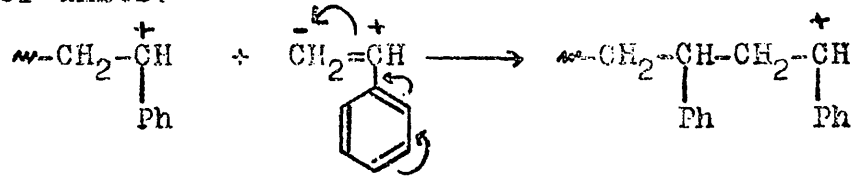
degradation features of [illegible] polystyrenes in order to collect as much information as possible about the weak links.

Kerr[28] pyrolysed a polystyrene sample prepared cationically. The system selected was styrene-stannic chloride in ethyl chloride, and he found that it degrades in exactly the same way as polymers prepared by free radical methods, showing the characteristic rapid fall in molecular weight at the beginning of the reaction, followed by the more gradual decrease when the weak link scission phase is complete. Kerr found that the weak link concentrations were 4.95×10^{-4} and 2.41×10^{-4} weak links per monomer unit of the ionic and free radical polymers respectively. The molecular weights were 129,600 and 130,200 and the temperatures of polymerization $-72^{\circ}C$ and $30^{\circ}C$ respectively.

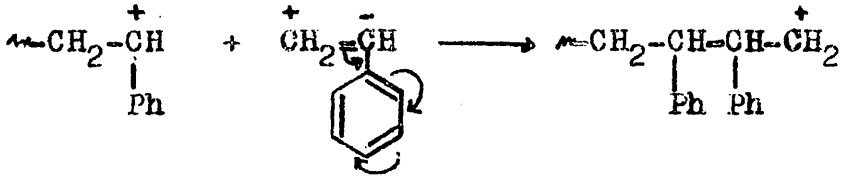
The initiation and propagation steps of cationic polymerization of styrene probably follow the mechanism outlined below[71]:-



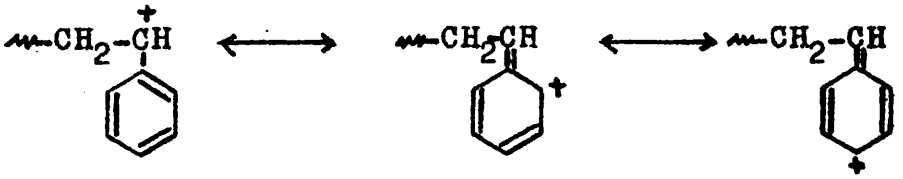
The benzene ring in the styrene molecule may act either as an electron source or acceptor[72], depending on the nature of the attacking reagent. If the attacking reagent were electrophilic, such as a carbonium ion, the phenyl group would be expected to act as an electron source, as shown, thus favouring a head to tail addition of monomer units:-



Polarization of the olefinic double bond in the opposite sense may be possible, however, due to the ability of the benzene ring to act as an electron acceptor, and thus would offer the opportunity for the head to head addition of monomer units:-

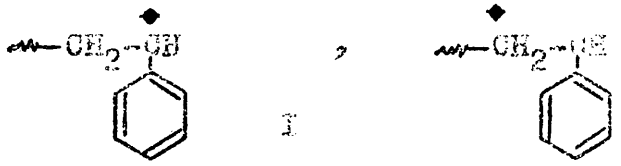


Head to tail addition would still be favoured from energy considerations because, as in free radical polymerization, resonance stabilization by the benzene ring of the electron deficient carbonium ion is possible:-



Head to head addition is less likely because the product radical has the free electron on the carbon atom β to the benzene ring and thus lacks the resonance stabilization

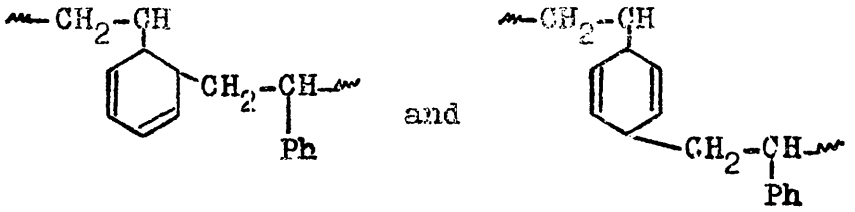
of radical I.



I II

From energetic considerations, therefore, head to tail additions are likely to predominate. Furthermore, steric considerations would favour a head to tail addition since the bulky phenyl groups would retard head to head addition. It follows that head to head addition would probably occur very infrequently during the polymerization.

The existence of such resonance structures will also render possible the propagation of the polymer chain through the ortho and para positions of the benzene ring giving rise to structures of the type:-



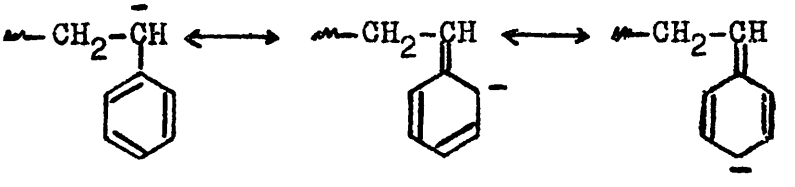
Thus the degradation behaviour of cationically prepared polystyrenes could be explained in terms of the same structures as proposed by Grassie and Cameron for free radical polymers.

Isotactic polystyrenes have also been thermally degraded[28,73,74] and perhaps surprisingly, exhibit the same features as other polymers prepared by free radical methods or cationically. However, the polymerisation

of isotactic polystyrene is also an ionic reaction and therefore may also result in abnormalities of the type just described, that is the formation of weak links is still possible despite the stereo-specific nature of the polymerization process, which would again suggest that the mechanism of degradation is similar to that occuring in these systems.

Cameron[75] degraded thermally and by ozone an atactic polystyrene sample prepared anionically with butyl lithium as catalyst. He found that the polymer responded to heat and ozone in exactly the same way as all the others which had been previously examined, showing the main features of the degradation, i.e. the initial steep fall in molecular weight indicating the presence of weak links. Moreover, he found that the weak link concentration lies within the range already observed for polymers prepared by free radical means.

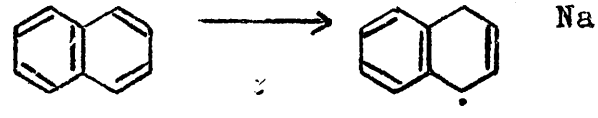
Again, Cameron suggested that analogous resonance behaviour can still take place, so that the presence of weak links in the polymer chains can be explained in terms of the same quinonoid structures as before:-



and the final conclusion drawn is that the same abnormalities could be responsible for weak links in polystyrenes

prepared by all three means; free radical, cationic and anionic.

Anionic polymerization has recently been of great interest in connection with the formation of "living polymers". Living polymers were first studied by Szwarc and co-workers[76]. Among anionic catalysts capable of producing living polymers is the sodium-naphthalene system[77,78]. The initiation and propagation steps of polymerization in this system might be represented as follows:-

<u>Catalyst formation</u>: $Na^{\bullet}$ +  Na^{+}

<u>Initiation</u>: Naphthalene^{-} + $CH_2{=}\underset{Ph}{CH} \longrightarrow \bar{C}H_2\text{-}\underset{Ph}{\dot{C}H} \leftrightarrow \dot{C}H_2\text{-}\underset{Ph}{\bar{C}H}$ + Naph. (I)

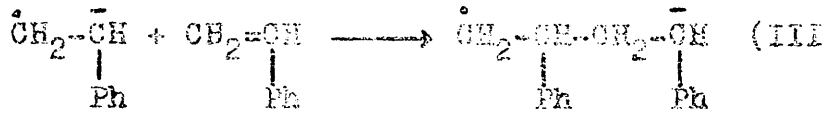
This electron transfer process leads to the formation of "radical-ion" species with some of the characteristics of a radical and of an anion. These monomeric radical-ions may either dimerize and continue their growth by anionic mechanism:-

<u>Dimerization</u>: $\dot{C}H_2\text{-}\underset{Ph}{\bar{C}H}$ + $\bar{C}H_2\text{-}\underset{Ph}{\dot{C}H} \longrightarrow \bar{C}H_2\text{-}\underset{Ph}{CH}\text{-}CH_2\text{-}\underset{Ph}{\bar{C}H}$ (II)

<u>Propagation</u>: $\bar{C}H_2\text{-}\underset{Ph}{CH}\text{-}CH_2\text{-}\underset{Ph}{\bar{C}H}$ + $CH_2{=}\underset{Ph}{CH} \rightarrow \bar{C}H_2\text{-}\underset{Ph}{CH}\text{-}CH_2\text{-}\underset{Ph}{CH}\text{-}CH_2\text{-}\underset{Ph}{\bar{C}H}$

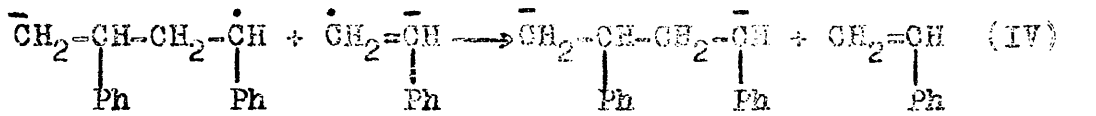
Or, on addition of one monomer molecule a "true radical-

ions" are formed:-

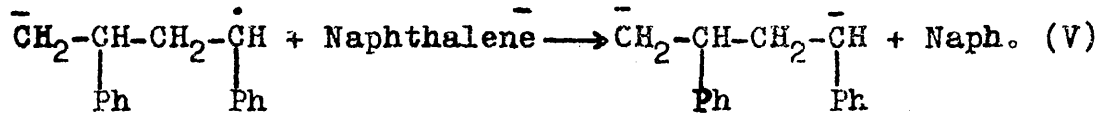


(III)

The radical ends of these dimeric radical-ions may either disappear, as shown in steps (IV) and (V) and continue their growth by the anionic mechanism:-



(IV)



(V)

Or, they may propagate polymerization from one end by a radical mechanism and from the other by the anionic mechanism. Therefore, these polymers possess active ends capable of further growth and is not terminated except on the addition of traces of hydroxylated substances such as water, alcohol.....etc. which give inactive anions.

A polystyrene prepared by this means might be expected to have different degradation characteristics from the others studied so far, especially in regard to the weak link scission phase of the reaction. For this reason it was decided to degrade "living" polystyrene samples prepared using the sodium-naphthalene catalyst system.

B. Change in Molecular Weight during Degradation:

The change in molecular weight with extent of volatilization which occurs during the bulk thermal degradation of "living" polystyrenes S_1, S_2 and S_3 at 350°C are shown in Fig. 25, together with data for the free radical styrene polymer S_4.

It is obvious that the main features of the degradation of the styrene polymers prepared anionically are exactly as before. These polymers responded to pyrolysis in the same way as those prepared by free radical and ionic mechanisms, showing the same characteristic drop in molecular weight in the early stages of the reaction, indicating the presence of weak links, followed by a gradual slow decrease with increasing extent of volatilization when the weak link scission phase is complete.

Thus it is apparent, as concluded by previous workers, that the two distinct and independent phases of weak link scission and depolymerization may be distinguished. Up to approximately 30-35% volatilization, the predominant reaction is weak link scission. Within the limits 30-100% volatilization it has been suggested that the gradual decrease in molecular weight with increasing extent of volatilization proceeds through a reverse polymerization mechanism initiated at the chain

ends. The change in molecular weight is accompanied by the production of volatile material through the depolymerization reaction. Thus the conclusion which must be drawn from these results is that the bulk thermal degradation of polystyrene prepared by ionic and free radical methods are essentially similar in both the weak link scission and volatilization phases.

Grassie and co-workers[28] have already shown that the later portion of the molecular weight / % volatilization curves lie between the horizontal and the diagonal running from the point of inflection at approximately 30-35% volatilization when weak link scission is presumed to be complete, to zero molecular weight and 100% volatilization. The implication of such a result has already been fully discussed in the case of the degradation of polymethyl methacrylate[15] when it was shown that it implies that on the average less than one stable involatile polymer residue remains per act of initiation at the chain ends of the polymer molecules. This in turn means that the zip length of reaction in which volatile products appear is longer than the chain length of the polymer molecule and most chains once activated will disintegrate completely to monomer before termination occurs. If all molecules unzipped completely the molecular weight / % volatilization curve would be parallel to the % volatilization axis, and the limiting value to which the molecular

weight would fall as a result of chain scission in the complete absence of depolymerization reaction, could have been directly obtainable. On the other hand, when the zip length of the reaction is less than the chain length of the polymer, then one involatile stable residue will remain of each polymer molecule activated, and the diagonal indicated above will be followed.

Recently Vink[79] studied the degradation of some linear polymers in aqueous solution. He offered an approximate mathematical treatment for the degradation process and developed theoretical curves showing the characteristics of the different modes of degradation; weak links, random scissions and zipping reactions.

According to this treatment, if degradation involves random scission of normal links a straight line will be obtained when $1/u_2$ is plotted against time, where u_2 is the ~~weight~~ average degree of polymerization. In the case of weak links randomly distributed along the polymer chain the initial slope of the curve is higher, decreasing to a constant value as the weak links are consumed. This constant value is characteristic of the degradation of the normal links. For a zip reaction the slope is initially lower, and increases with time.

The results of the present work are plotted as the reciprocal of the change in molecular weight during degradation against extent of volatilization, for polymers S_1, S_2, S_3 and S_4, in Fig. 26.

If the assumption made in Vink's mathematical treatment is applicable, then Fig. 26 shows that all styrene polymers studied have weak links, since, up to 30-35% volatilization, the curves are slightly convex upwards. From 30-100% volatilization the curves are concave upwards, indicating that a zip reaction is taking place from the polymer chain ends. This picture is in general agreement with previous work. Data for the degradations of these polymers are summarized in Tables 14-17.

C. Production of Volatiles during Degradation:

It was pointed out in Chapter 1 that considerable amounts of fragments larger than monomer such as dimer, trimer, tetramer and pentamer, along with monomer constitute the volatile products formed during the bulk thermal degradation of polystyrene in vacuum. Monomer is produced by depropagation from long chain radicals, while non-monomeric volatile products are produced by intramolecular transfer from the same long chain radicals.

The products volatile at room temperature constitute about 42% of the products volatile at the degradation

Table 14

Thermal Degradation of Polymer [illegible]

Initial $\bar{M}_n$. 255,000

Time of heating (mins.)	Extent of Volat. %	$\bar{M}_n$ Wt. $\times 10^{-3}$	% Vol. at A.T. (Room temp)	Wt ratio, Non-condensable Monomer in products.	$n \times 10^3$ (n = weak links per monomer unit)
2	1.2	173	-	-	0.19
4	1.6	140	-	-	0.32
13	1.8	114	-	-	0.49
30	5.9	75	-	-	0.90
45	6.5	68	-	-	1.02
60	14.4	52	-	-	1.31
75	18.8	48	-	-	1.35
95	32.4	40	-	-	1.35
106	37.6	26	-	-	2.10
120	39.5	23	-	-	2.33
90	39.5	20.5	-	-	2.66
105	50.1	-	40.9	1.4	-
155	63.0	17	44.5	1.25	1.86
180	63.2	17	37.4	1.7	1.85
150	63.3	12	37.1	1.7	2.78
210	64.9	15	-	-	2.03
210	71	12.5	43.7	1.3	2.01
240	78.8	12	-	-	1.43
300	85.8	11.2	-	-	0.91

Table 15

Thermal Degradation of Polymer [illegible]

Initial M.Wt. 495,000

Time of heating (mins.)	Extent of Volat. %	M.Wt. $\times 10^{-3}$	$x \times 10^{3}$
5	2.4	175	0.37
15	2.9	195	0.31
30	3.7	146	0.48
40	7.9	83	0.94
35	10,9	66	1.19
60	11.1	65	1.21
50	13.0	55	1.44
71	18.8	44	1.71
120	22.5	48	1.47
90	24.6	37.5	1.88
90	33.5	32	1.96
100	44.0	26	2.03
100	44.9	25	2.09
120	47.9	23	2.15
150	48.1	24.5	2.0
105	51.3	23	1.99
182	69.5	17	1.66
180	72.7	18.5	1.32
210	78.6	17	1.10

Part 15

Thermal Degradation of polymer S_2 at 350°C.

Initial M.Wt. 511,000

Time of heating (mins.)	Extent of Volat. %	M. Wt. x 16^{-3}	% Volat. at R.T.	Non monomer/ Monomer	n x 10^3
15	2.5	98.5	-	-	0.86
30	6.0	75	-	-	1.13
60	13.4	48	-	-	1.71
75	19.4	40	-	-	1.93
90	38.6	27	45.3	1.2	2.20
150	52.2	24.5	38.9	1.6	1.86
210	76	15	40.3	1.5	1.49
270	89.7	10	-	-	0.91

Table IV

Thermal Degradation of Polymer [illegible]

Initial M.Wt. 5,000.00

Time of heating (mins.)	Extent of Volat. %	M. Wt. x 10^{-3}	% Volat. at R.T.	Non-volatile/ Monomer	n x 10^2
128	12.8	64	-	-	1.40
267	22.6	37	-	-	2.16
256	23.3	34	-	-	2.33
255*	73.0	19	40.2	1.5	1.46

* This experiment was carried out at 346°C.

Figure 25

Change Of Molecular weight with Extent Of Volatilization.

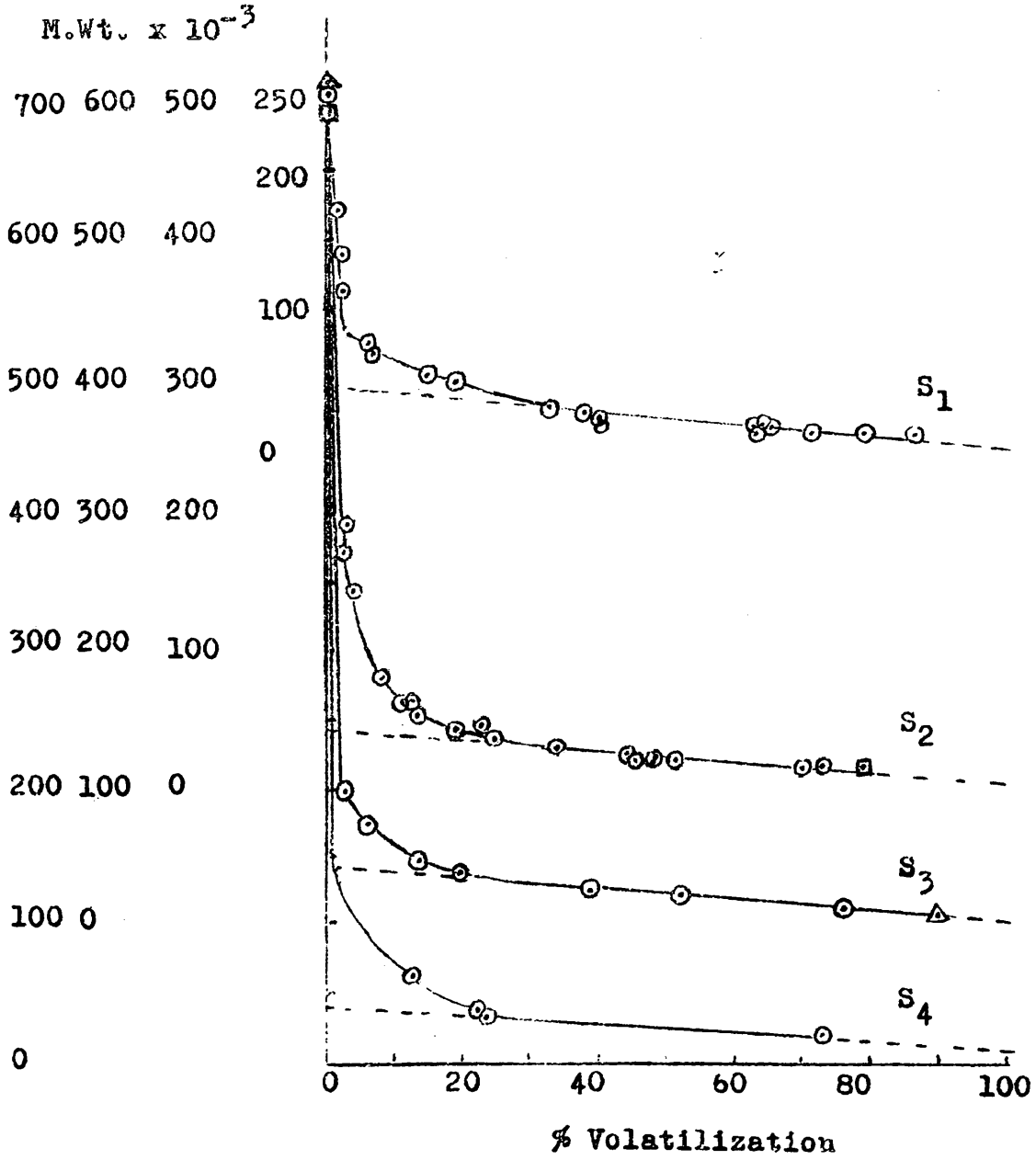
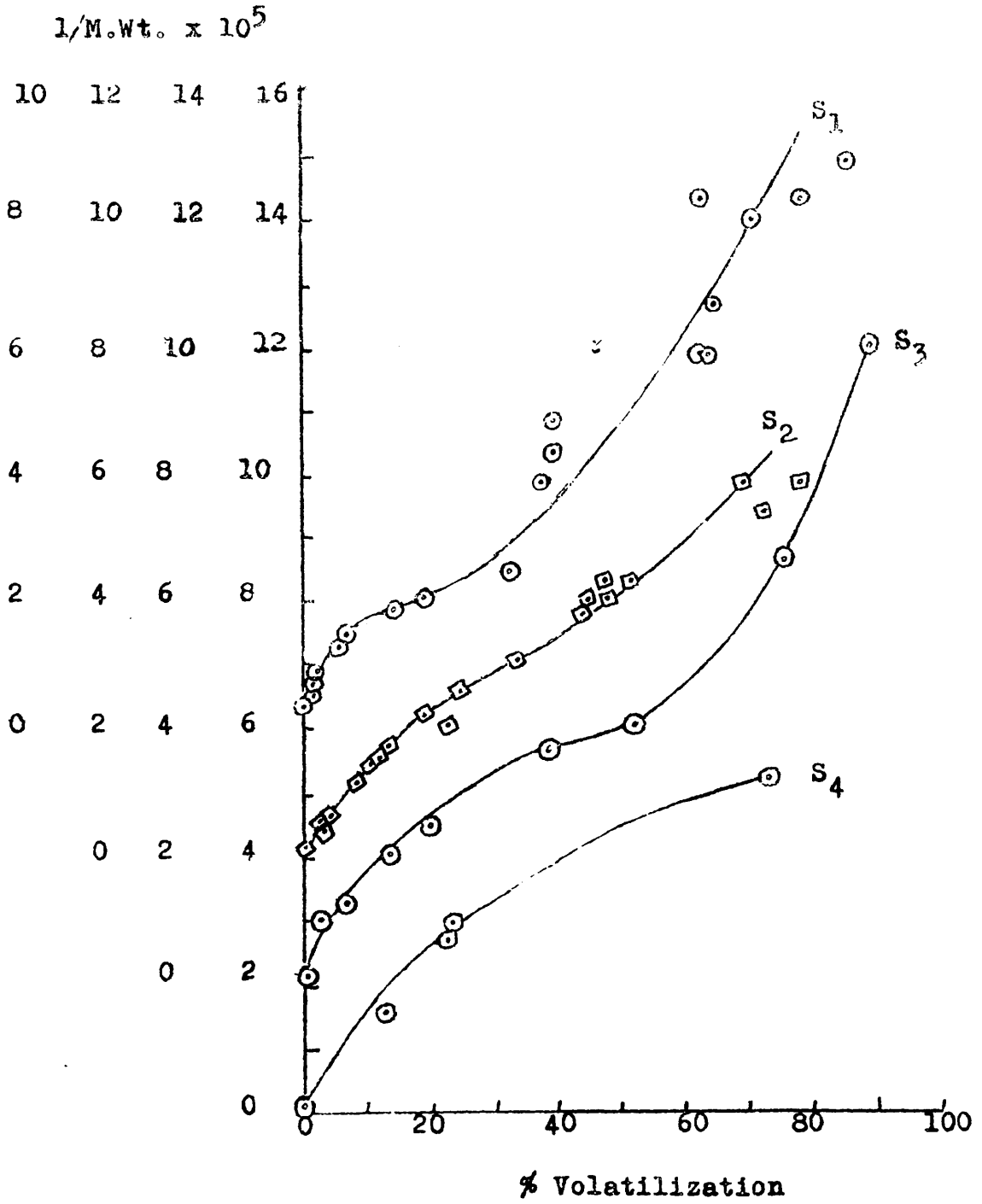


Figure 26

Change Of 1/M.Wt With Extent Of Volatilization



temperature, of which approximately 40% is monomer and the remainder is small quantities of toluene and traces of ethyl benzene and methyl styrene. Dimer and trimer are present in approximately the same yield, while tetramer and pentamer are present only in very small amounts. Grassie[27] suggested that , since the order of abundance is dimer, trimer, tetramer and pentemer, the nearer the radical chain end is to the centre at which transfer occurs, the easier it is for the chain end intramolecular transfer process to take place. Thus the overall energy requirements for the reaction to occur in the same molecule are very much less than could be necessary for an intermolecular transfer process, and it seems that there will be a large probability of internal energy transfer between the bonds made and broken in the same molecule, facilitating the intramolecular process.

The yields of products volatile at room temperature together with the ratios of non-monomer to monomer, at various stages of the degradation reaction, are also quoted in Tables 14-17. As indicated in these Tables, the yield of material volatile at room temperature is on the average about 41% of the volatilized part. Moreover the ratios of non-monomer to monomer produced at various stages during the degradation reaction, remains sensibly constant throughout the course of the reaction at a fixed temperature.

D. Rate of production of volatile Material during Degradation:

The plots of extent of volatilization as a function of time of degradation are shown in Fig. 27. Also the change in relative rates during degradation with extent of volatilization, are illustrated in Fig. 28.

Fig. 27 indicates that there is no inhibition period in the initial stages of the degradation reaction.

Fig. 28 shows that the rate of production of volatile material reaches a maximum in the range of about 35-40% volatilization at 350°C, and 25-30% volatilization at 330°C. Madorsky[24,80] found similar effects in investigating the thermal degradation of styrene polymers prepared thermally by free radical methods, but he offers no explanation.

Thus it can be concluded from the above results that the range where the maximum rate of production of volatile material reaches, at one fixed temperature, in the the bulk thermal degradation of polystyrene, is independent of the molecular weight of the polymers and of their mode of preparation.

The occurence of a rate maximum in the degradation reaction of polystyrene is explained by Grassie and

co-workers[29] who assumed on the basis of their results that weak link scission and depropagation are two separate and independent processes. The former occur at random along the polymer chain and result in the production of stable molecules with single and double bonded chain ends, which subsequently degrade, and the latter at the chain ends, leading to the production of volatile material, monomer to pentamer, in a reverse polymerization reaction and an intramolecular transfer process respectively. Thus the increase in the rate of production of volatile material and consequently the rate maximum observed during the reaction was explained by the above authors on the basis of the increasing number of degradable chain ends produced during the chain scission phase of the reaction. The maximum number of degradable chain ends will be present when the chain scission is just complete at approximately 30% volatilization.

Simha and Wall's[23] theoretical expression for the rate of conversion of a polymer to volatile material for a purely random process, predicts a rate maximum at 25% conversion, when the chain length N of the starting material is very much greater than L, which is defined as the number of units in the smallest chain which does not evaporate before being further degraded.

These authors claimed that the maximum rate is an indication that the total number of molecules between the sizes L and N reaches a maximum, and that this extreme is characteristic of the random scissions of linear chains. They also showed that the conversion at which the maximum rate occurs is not affected very much by the magnitude of L. Moreover, they showed that in a degradation reaction with a short kinetic chain length the rate is practically linear with extent of conversion, while with large kinetic chain lengths curvature appears.

The difference between the theoretical figure of 25% conversion and Madorsky's experimental value of 35-40% volatilization is explained by postulating that in polystyrene the phenyl groups apparently stabilize the styrene radical to such an extent that a good monomer yield is obtained although the reactive hydrogens for transfer reactions are present. Thus polystyrene degradation results do not correspond to pure random mechanism, since large amounts of monomer are formed for a relatively small decrease in molecular weight. By considering the ratio between monomer and all other volatilized material they came to the conclusion that the degradation of polystyrene has a kinetic chain

length of the order of three, that is very small, but that it differs sufficiently from unity to make the process not pure random. Later Grassie and Kerr[29] have demonstrated that the reaction has a chain length of the order of 10^3.

Taking the above considerations in mind, then according to Simha and Wall's theoretical treatment, it appears that the kinetic chain length of the thermal degradation of the styrene polymers studied is long, since the plots of relative rates of degradation against extent of volatilization are not straight lines, but show curvature. Moreover, it can be deduced from Fig. 28 that the height of the maximum rate is a function of the degradation temperature, increasing with rise of temperature of degradation. Since it is assumed to increase proportionally with L, this would seem to indicate that the higher the temperature of degradation the larger the size of molecules which can evaporate without being further degraded. Grassie and Kerr suggested that the concentration of weak links is independent of degradation temperature, and that the rate maximum is an indication of the presence of a maximum number of degradable chain ends, thus the small tendency of the rate maximum to shift to lower conversion, at lower temperatures, can be accounted for in terms of a small

decrease in the rate of production of volatile material, i.e. a small decrease in the rate of monomer producing and intramolecular transfer processes.

E. Temperature Programmed Degradation:

Some experiments have been carried out on the temperature programmed degradation apparatus, previously described in Chapter 2.

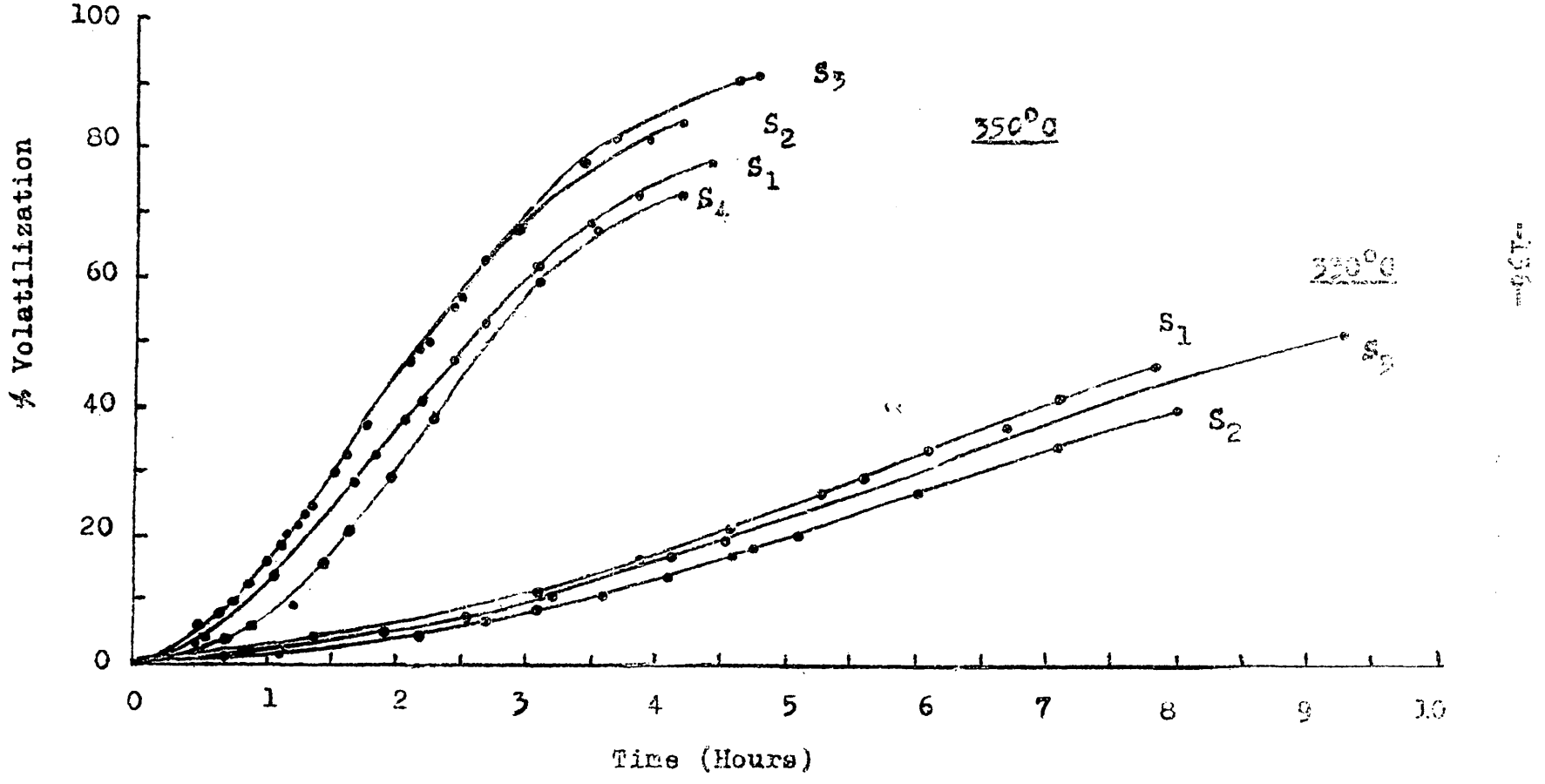
The curves obtained, which represent pressure, as measured by a pirani gauge, versus the temperature of degradation, at a constant rate of $10^{o}C$/min., are shown in Fig. 29. The production of volatile material begins at approximately $300^{o}C$. and is quite slow up to $330^{o}C$., when it increases rapidly to a maximum at $410^{o}C$.

The almost identical curves for polymers S_1 and S_3 (anionic) and polymer S_4 (free radical) indicate that these polymers have nearly the same thermal stability irrespective of their molecular weights and the mode of preparation.

F. Estimation of the Number of Bonds Broken:

Grassie and Kerr[29] and later Grassie and Cameron[75] used the following relationship in estimating the number of weak links S, originally present in a styrene polymer

Figure 27


100
80
60
40
20
0
% Volatilization
0
1
2
3
4
5
6
7
8
9
10
Time (Hours)
S3
S2
S1
S4
350°C
S1
S2
S2

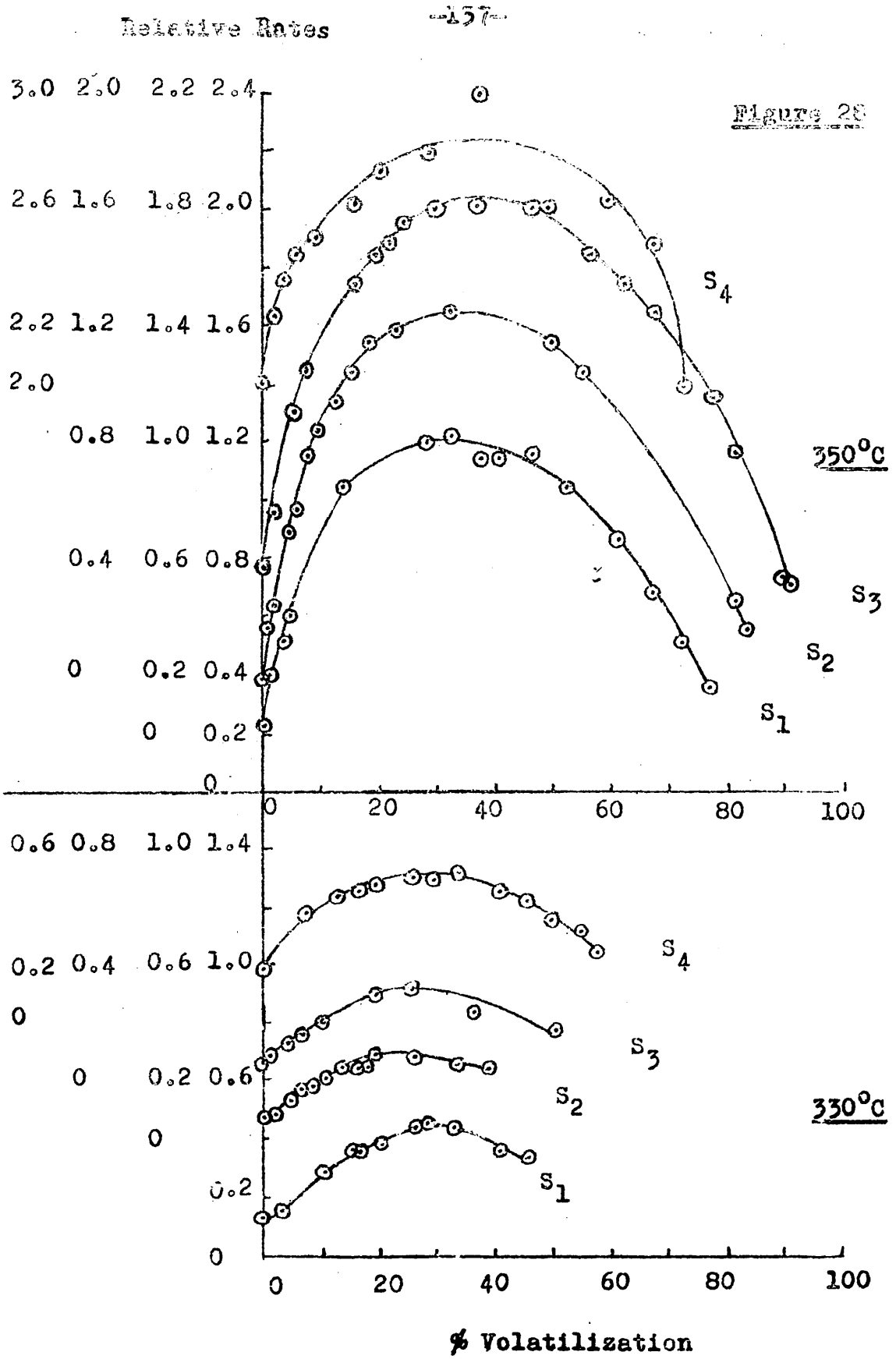
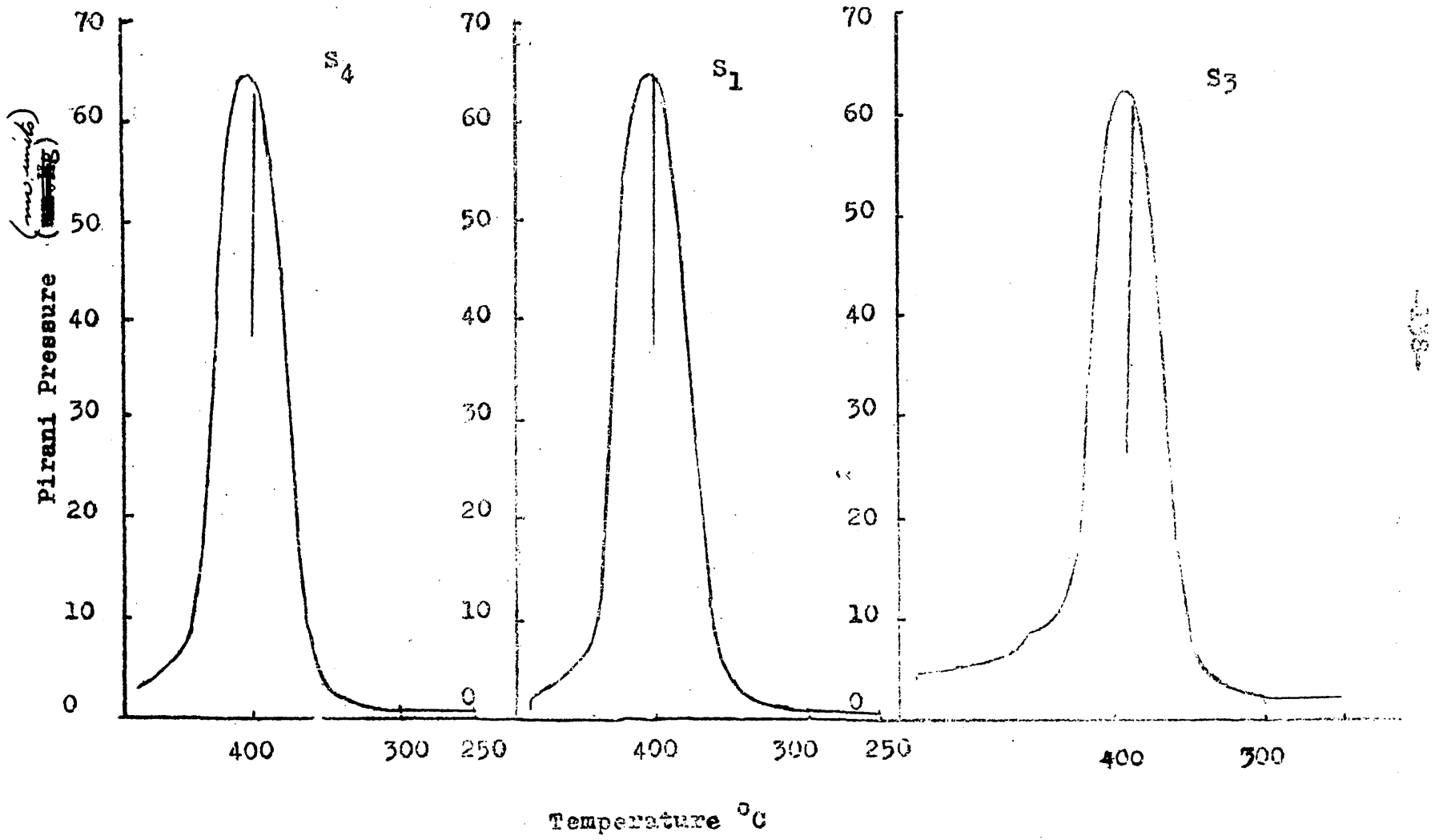

Relative Rates
3.0 2.0 2.2 2.4
2.6 1.6 1.8 2.0
2.2 1.2 1.4 1.6
2.0
0.8 1.0 1.2
0.4 0.6 0.8
0 0.2 0.4
0 0.2
0
0 20 40 60 80 100
S4
S3
S2
S1
350°C
0.6 0.8 1.0 1.4
0.2 0.4 0.6 1.0
0
0 0.2 0.6
0
0.2
0
0 20 40 60 80 100
S4
S3
S2
S1
330°C
% Volatilization

Figure 28

Figure 29

Temperature Programmed Degradation Curves



molecule:-

$$S = M_o/M_d - 1$$

and consequently the number of bonds broken, N, per polymer chain is given by:-

$$N = Cl_o/Cl_d - 1$$

where M_o and Cl_o are the average number molecular weight and chain length of the undegraded polymer, and M_d and Cl_d are the limiting values to which the molecular weight and chain length of the polymer would fall as a result of chain scission, in the complete absence of depropagation.

As the number of weak links present in polymers of different molecular weights will have to be compared it is more convenient to discuss the results in terms of the number of weak links present per monomer unit, n, which is independent of the molecular weight of the polymer, and is given by:-

$$n = M\ (1/M_d - 1/M_o)$$

and $$n = 1/Cl_d - 1/Cl_o$$

and consequently $N = n.Cl_o$

The value of M_d for each of the polymers studied was obtained from the molecular weight/extent of volatilization curves(Fig. 25) by extrapolation back to zero extent of volatilization from the linear portion beyond 30-35% volatilization, at which the chain scission phase of the

reaction is assumed to be complete.

An alternative method was also used. The number of bonds broken, S, per polymer molecule and N, per polymer chain, are given by:-

$$S = M_o(1-x)/M_t - 1$$

and

$$N = Cl_o(1-x)/Cl_t - 1$$

where M_o, Cl_o and M_t, Cl_t are the molecular weight and the chain length of the undegraded polymer and of the degraded polymer at the degree of volatilization x.

Since

$$N = n.Cl_o$$

the number of weak links, n, present at time t per monomer unit is given by:-

$$n = M\left[(1-x)/M_t - 1/M_c\right]$$

and

$$n = (1-x)/Cl_t - 1/Cl_o$$

The number of weak links originally present in a polystyrene sample can be obtained directly from the number of bonds broken/extent of volatilization curves from the point 30-35% volatilization at which the curve begins to flatten out or reach a maximum, as shown in Fig. 30. The results are summarized in Tables 14-18, from which it can be seen that there is a good agreement between the values of weak link concentration calculated on the basis of the two methods.

The shape of the curves in Fig. 30 shows that the number of bonds broken due to the presence of weak

links distributed at random along the polymer chain, increases with extent of volatilization till it reaches a maximum. Beyond the maximum the rate decreases gradually which may be attributed to the complete removal of some of the shorter chains by unzipping.

More recently Farish[81] thermally degraded a polystyrene sample prepared at 60°C with (AIBN) as a free radical initiator. The polymer had an initial molecular weight of 73,000. The results obtained by this author are also quoted in Table 18 as polymer S_5, and show that the concentration of weak links is of the same order of magnitude as that for ionic and free radical polymers used in the present work.

Though there appears to be a slightly greater concentration of weak links in polymer S_4, as illustrated in Fig. 30, the results of its degradation are not so reliable, especially in the region of extrapolation, since no degradation experiments have been carried out in the range of 25-70% volatilization. It was not possible to determine completely the molecular weight/conversion curve. It does mean, however, that some doubt remains as to whether the extent of chain scission may depend upon molecular weight.

The results of Kerr and Cameron summarized in

Table 18 show lower values for weak link concentration which indicates that their molecular weight values are high, and consequently there will be a tendency for their extrapolated M_d values to be higher. This could easily be due to the different apparatus used for the determination of the number average molecular weight of the polymers. These authors used a modified form of the Fuoss-Mead[82] osmometer with a bacterial cellulose membrane, while in the present work as previously mentioned in Chapter 2, and also in the work done by Farish, a high speed membrane osmometer was used[91]. This latter osmometer has a small membrane area and equilibrium is attained in a very short time, so that the time of measurement is short. Thus it is less subject to errors due to diffusion of polymer through the membrane.

G. Determination of the Activation Energies:

Varying results for the activation energy have been previously reported. Jellinek[13,14] reported for the thermal degradation of polystyrene an activation energy of 44.7 k.cal/mole in the range of 15-80% volatilization. For the same conditions, Atherton[83] obtained 50 k.cal/mole. Madorsky[24] found 58 k.cal/mole for the initial stages of the reaction, reducing to 56 and 54 k.cal/mole at 25 and 50% volatilization. Zemany[20] has reported a higher energy of activation of 65k.cal/mole at extents

Figure 30

Change Of Number Of Bonds Broken / Chain Unit

With Extent Of Volatilization

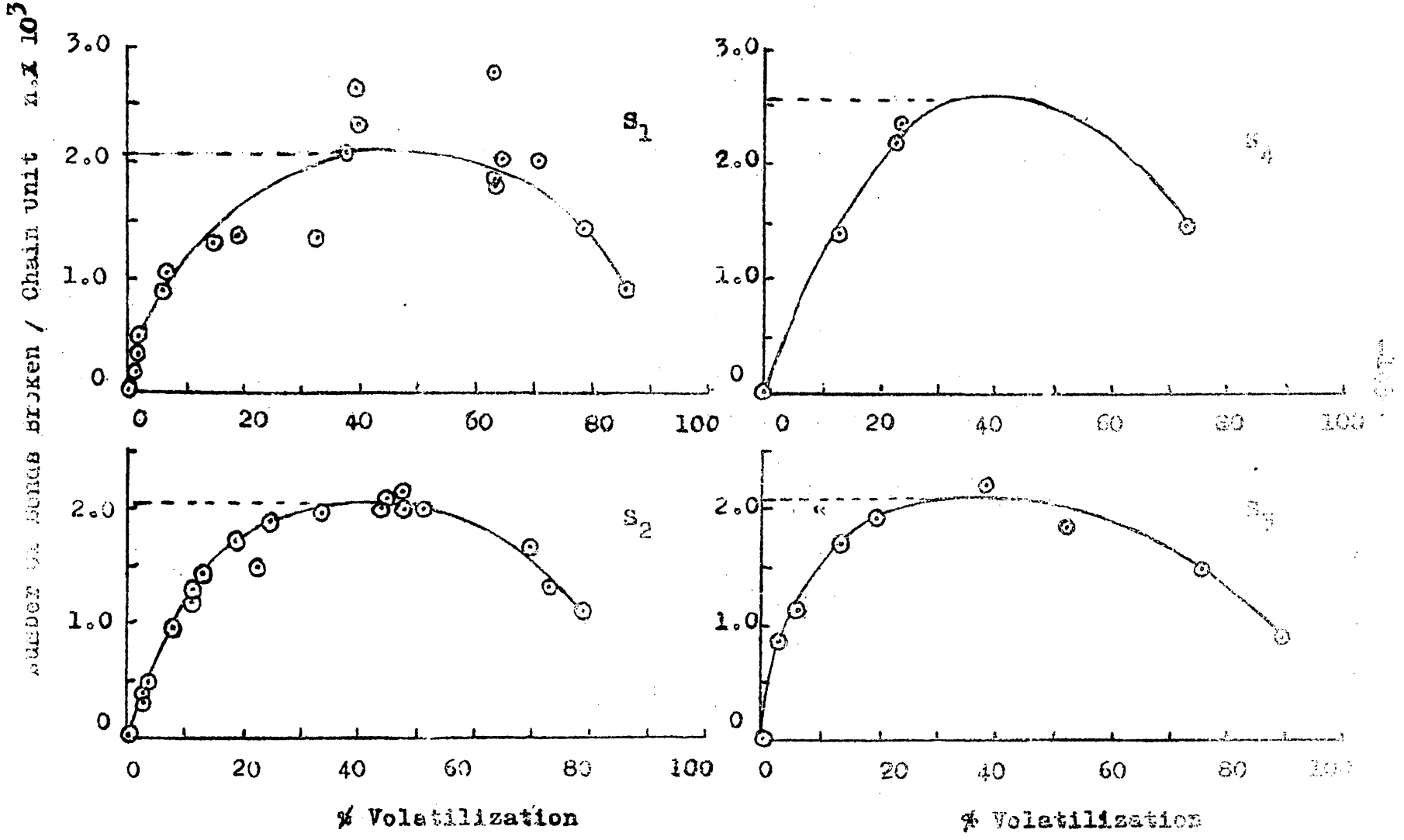


Table 18

Data of Weak Link Concentration for Polystyrenes.

Polymer	Mode of prep.	Temp. of Degr. °C	M_o x10^{-3}	M_d x10^{-3}	n^a x10^3	n^b x10^3	Ref.
S_1	Anionic	350	255	45	2.16	2.06	present
S_2	"	"	495	44	2.16	2.05	"
S_3	"	"	611	44	2.20	2.08	"
S_4	Free R.	330	5,000	40	2.58	2.505	"
S_5	"	320	73	14	1.53	-	81
S1159	Anionic	335	570	113	0.71	-	75
S/GG/5	Free R.	"	530	100	0.84	-	"
	Cation.	290	129.6	80	0.50	-	28
S_7	Free R.	"	640	118	0.72	-	"

a Data obtained by extrapolation of molecular weight/extent of volatilization curves.

b Data obtained by extrapolation of number of bonds broken per chain unit/extent of volatilization curves.

of reaction less than 1%. Montgomery and Winkler[84] found 40 k.cal/mole. In a thermogravimetric study of polystyrene, Anderson and Freeman[85] obtained an activation energy of 46 k.cal/mole up to approximately 10% volatilization, and 60 k.cal/mole for the range of 15-95% conversion. They suggested that the activation energy is a function of the degradation temperature. Recently Nakajima, Hamada and Skimizu[74] investigated the thermal degradation of isotactic polystyrene, and found an activation energy of 42 k.cal/mole.

In the present work the activation energies were obtained by plotting the logarithm of the initial rates, for different extents of the degradation reaction and at various temperatures as a function of the reciprocal of the absolute temperature. The results obtained are summarized in Table 19 and illustrated in Fig. 31.

The initial rates of degradation have been measured during the period of heating up the polymer to the required temperature, while the rates at different extents of volatilization were measured while the system was cooling down.

It can be seen from the results in Table 19 that at high conversions the degradation reaction has an activation energy of approximately 44 and 34.5 k.cal/mole for anionic and free radical polymers respectively.

(Fig.31 -c-).

At lower extent of volatilisation [illegible] energy for the reaction is approximately 30 k.cal/mole for anionic polymers (Fig. 31 -b-).

These energies of activation obtained in the range 39-91% volatilisation probably correspond to the depolymerization reaction only, since weak link scission is assumed complete at this stage.

In the initial stages of the reaction an average value of 18 k.cal/mole was obtained for anionic polymers, and 12.5 k.cal/mole for free radical polymers (Fig.31-a-). However, it is doubtful what this energy of activation is really measuring, since in the initial stages of the reaction the number of degradable molecules is continuously increasing as the weak links are being progressively broken.

H.Conclusion:

The principal features of the degradation of polystyrene do not seem to depend on the method of preparation of the polymer. In all cases the molecular weight falls off rapidly up to approximately 30% volatilization and the maximum rate of production of volatiles occurs at the point at which the rapid decrease in molecular weight ceases.

Figure 31 (b)

Activation Energies

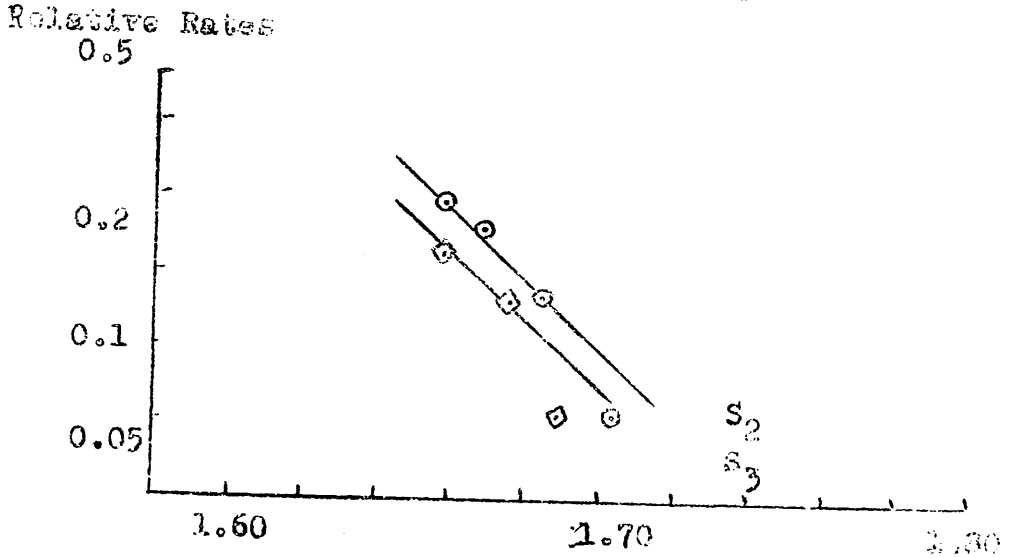


Figure 31 (a)

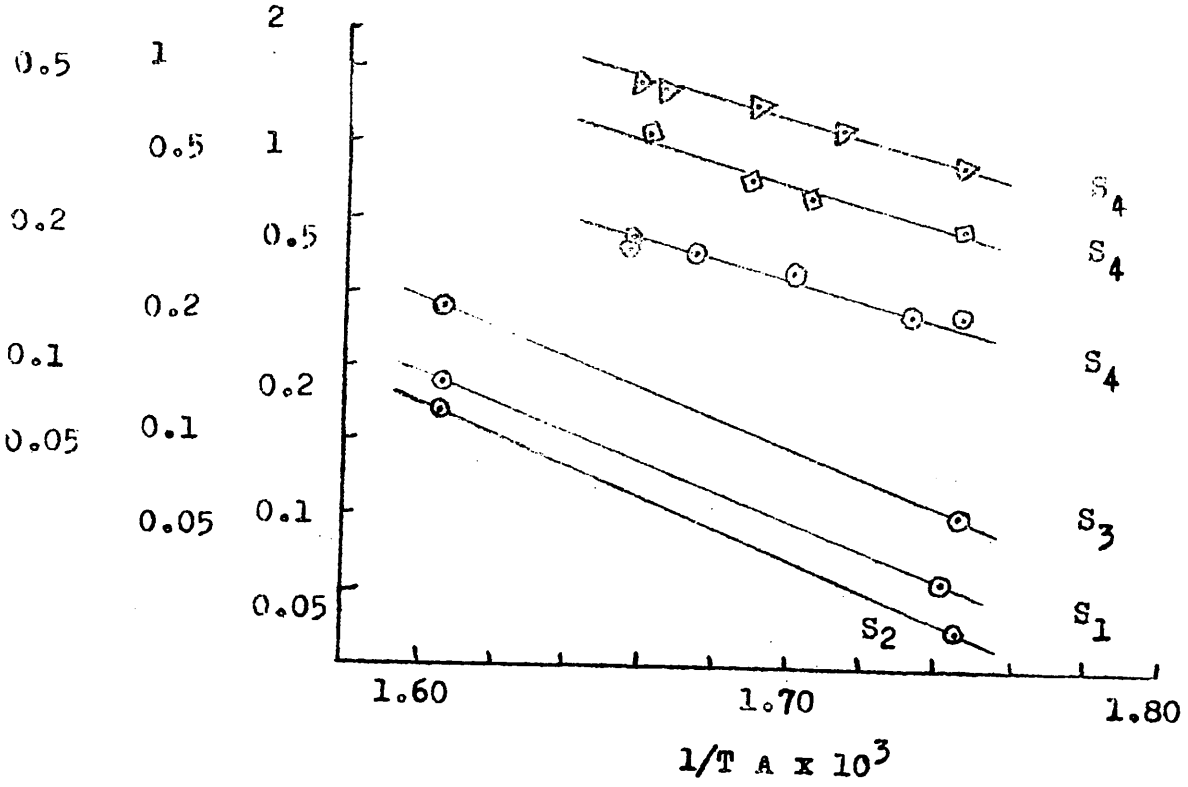


Figure 31 (c)

Activation Energies

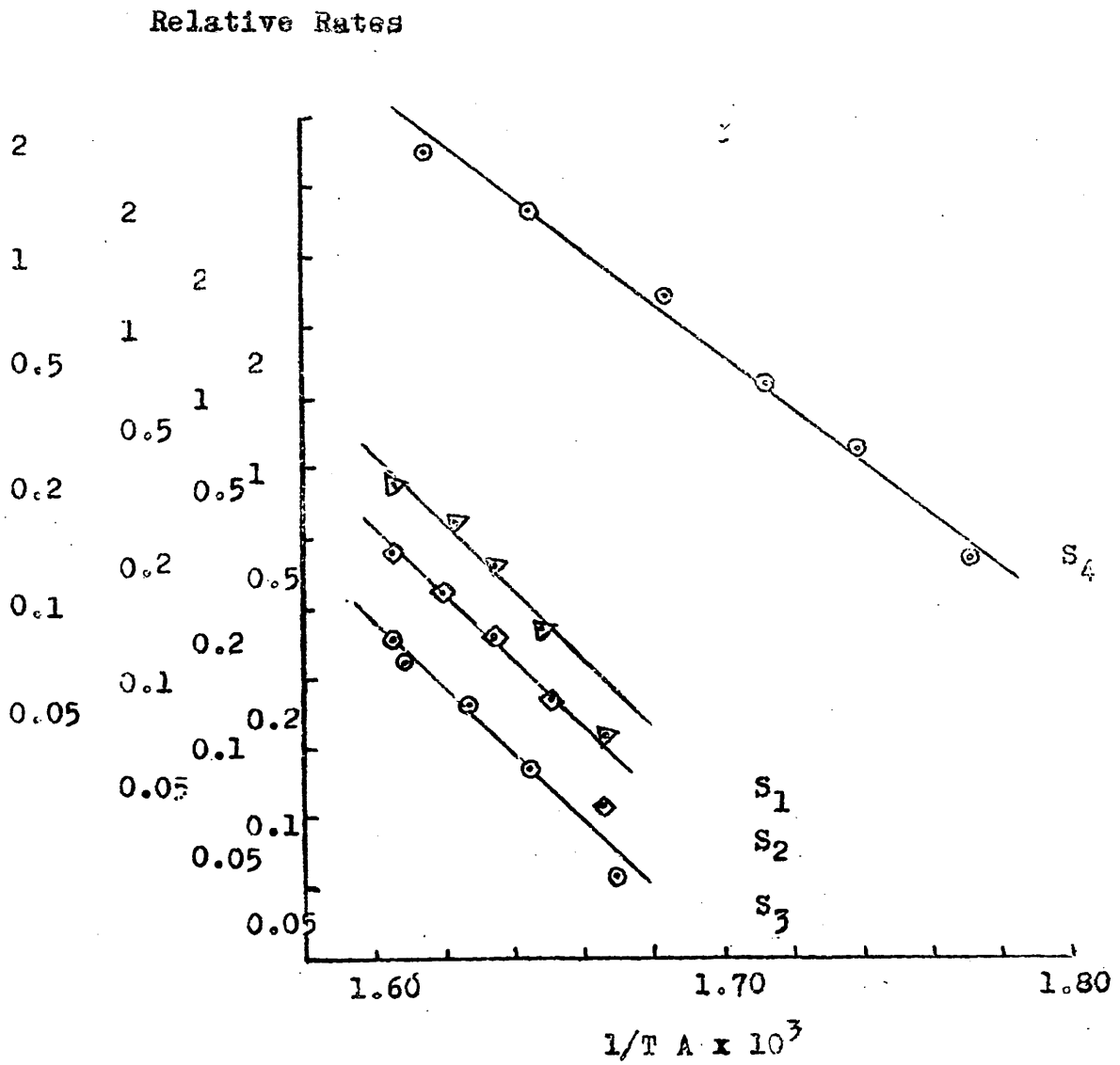


Table 19

Activation Energies.

Polymer	Mode of prepn.	M_o x 10^{-3}	Temp. range °C.	Extent of Volat. %	Activation energy k.cal/mole.
S_1	Anionic	255	300-350	Initial	17.8
"	"	"	320-350	77.2	44.7
S_2	"	495	300-350	Initial	19.1
"	"	"	306-330	39.1	42.7
"	"	"	320-350	83.4	43.9
S_3	"	611	300-350	Initial	18.0
"	"	"	310-330	50.5	41.2
"	"	"	313-350	91.1	44.5
S_4	Free R.	5,000	300-331	Initial	12.4
"	"	"	300-331	"	12.4
"	"	"	300-330	"	12.8
"	"	"	270-350	73.0	34.6

Comparison of the weak link concentration in a variety of polystyrenes from Table 18 shows that the weak link concentration of "living" polymers is of the same order as already observed for polymers prepared by free radical means. This seems rather surprising. According to Grassie and Kerr's[29] assumption that weak links are formed in some process which competes with the normal propagation reaction during polymerization, and which has slightly higher energy of activation, then from the different modes of preparation of these polymers a wider variation in weak link concentration might reasonably have been expected.

CHAPTER 5

THERMAL DEGRADATION OF FREE RADICALLY PREPARED METHYL RING-SUBSTITUTED POLYSTYRENES

A. Introduction:

It is clear from the discussion in Chapter 1 that either of the two proposed theories, involving weak links or intermolecular transfer, could account for the rapid fall in molecular weight in the initial stages of the thermal degradation of polystyrene. The available evidence, however, does appear to favour the weak link theory.

The evidence produced by Grassie and co-workers supports the idea of scission at a limited number of weak links distributed at random along the polymer chain, rather than intermolecular transfer of a depolymerizing radical with another polystyrene molecule leading to a subsequent scission of that chain.

The intermolecular transfer theory implies that the production of volatile material and the chain scission process are parts of the same overall radical reaction, and may be regarded as two competing depropagation steps. On the other hand, according to the weak link theory the production of volatile material and the initial steep fall in molecular weight are two separate and independent

processes. Moreover, Grassie and Cameron have shown that weak links in polystyrene are associated with unsaturation in the main polymer chain, because double bonds exist in the same concentration as thermo-labile links.

In spite of all this information, however, the exact chemical nature of the weak links and their mode of formation is still not known, although a number of suggestions have been made. One of the more likely proposals suggested by Grassie and Cameron is that weak links are quinonoid structures. If weak links are formed in this way and have that sort of structure, then one would expect that substitution in the benzene ring would have a marked influence on the mode of formation and decomposition of weak links.

Thus, styrenes substituted in the ortho and para positions might yield a completely normal polymer, devoid of weak links, as bulky groups in these positions might effectively hinder abnormal additions. This led to the idea of examining the thermal degradation of methyl ring-substituted styrenes, though it was by no means certain that methyl groups are sufficiently bulky to give complete steric hindrance. Nevertheless, such polymers might conceivably contain a lower concentration of weak links than the normal polystyrene.

Since there is a close relationship between polymerization and some degradation features, the polymerization kinetics of methyl substituted styrene monomers have been studied, as described in Chapter 3. As a sequel to this work the thermal degradation of mono- and di- and trimethyl substituted styrene polymers have been studied and are described in the following sections.

B. Temperature Programmed Degradation:

The results obtained from experiments carried out on the temperature programmed degradation apparatus are shown in Fig. 32. The curves obtained represent pressure as measured by a pirani gauge, versus the temperature of degradation, which increases at a constant rate of 10°C/minute. The curves indicate that the methyl ring-substituted styrene polymers are less thermally stable than polystyrene, illustrated in Fig. 29, Chapter 4, since they start to degrade at lower temperatures.

For P- and M-methyl styrene polymers the production of volatile material begins at approximately 250°C and is quite slow up to about 300°C, then increases rapidly to a maximum at 390°C. For O-, 2,4-di, 2,5-di, and 2,4,6-trimethyl styrene polymers production of volatiles begins at about 225°C, then begins to increase

rapidly at approximately 250°C for O-, 2,4-di and 2,5-di methyl styrene polymers, and at 275°C for the 2,4,6-tri methyl styrene polymer. For all four polymers the production of volatiles reaches a maximum at about 370°C.

It is thus clear that the order of decreasing thermal stability for the mono-substituted polymers is:-

PMS ≏ MMS > OMS

The di- and tri-substituted polymers have approximately the same thermal stability. Yet, from Fig. 32 it could be observed that the overall order of stability may be written as follows:-

PMS ≏ MMS > 2,4,6-Tri.MS > OMS ≏ 2,4-Di.MS ≏ 2,5-Di.MS

The general conclusion which can be drawn from these results is that the thermal stability of methyl ring-substituted styrene polymers is lower than that of styrene polymers, and depends upon the position and number of methyl groups located in the benzene ring. The introduction of even one methyl group in the ortho position markedly increases the ease of decomposition.

C. Change of Molecular Weight during Degradation:

Fig. 33 illustrates the change in molecular weight which occurs with the extent of volatilization during the bulk thermal degradation of methyl styrene polymers studied at 330°C. The data obtained are summarized in

Figure 32 (a)

Temperature Programmed Degradation Curves

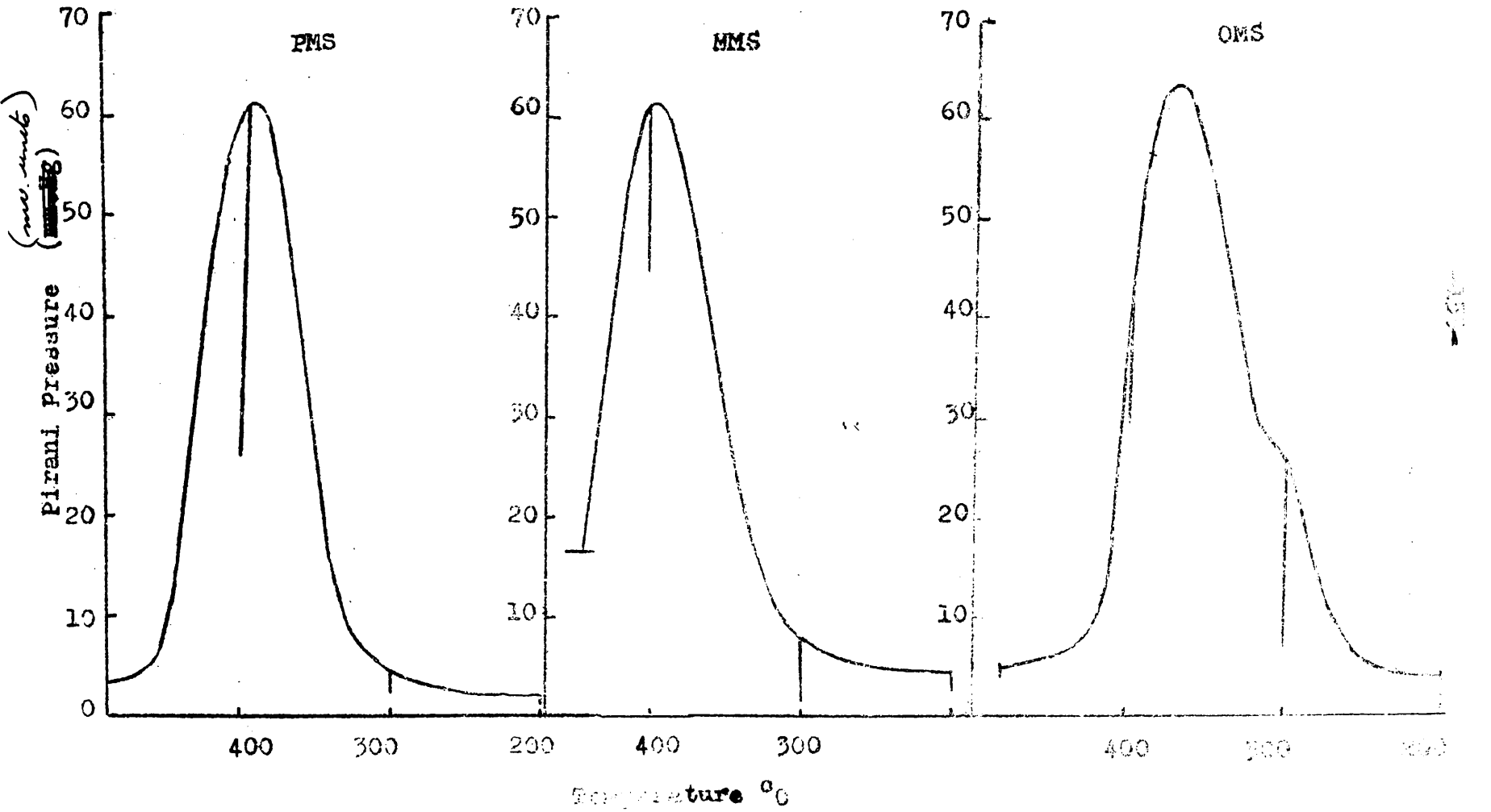
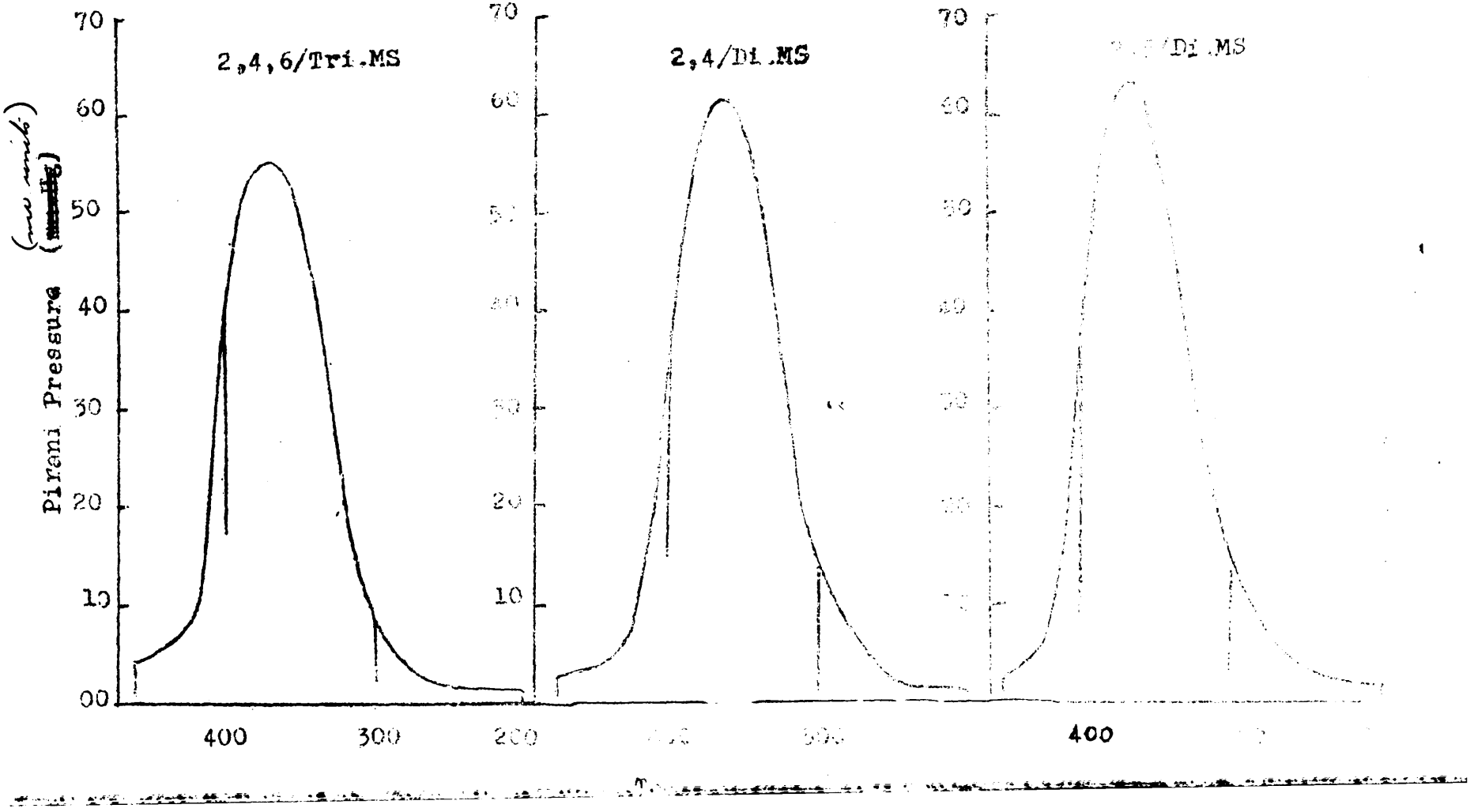


Figure 32 (b)

Temperature Programmed Degradation Curves



Tables 20-23.

The experimental results indicate that the main features of the thermal degradation of the styrene polymers investigated by previous workers and of those studied in Chapter 4 remain anchanged, inspite of the introduction of methyl groups at various positions in the styrene benzene ring. Fig. 33 shows the characteristic steep fall in molecular weight in the early stages of the reaction, up to approximately 25-30% volatilization, which is assumed to indicate the presence of weak links along the polymer chains. When this weak link scission phase is complete, there is the gradual decrease in molecular weight with increasing extent of volatilization, which could be attributed, as in the case of polystyrene, to a reverse polymerization mechanism initiated at the chain ends.

The later portion of the molecular weight/extent of volatilization curves follow the diagonal running from the point of inflexion at approximately 25-30% volatilization, to zero molecular weight and 100% volatilization. This implies that the zip length of the reaction is less than the chain length of the polymer molecule, so that one involatile stable residue will remain from each polymer molecule activated, while in

the case of polystyrene this portion lies between the horizontal and the diagonal, so that the zip length of the reaction is longer than the chain length of the polymer molecule.

According to Vink's[79] mathematical approach Fig. 34 shows that the methyl styrene polymers studied have weak links, since the curves are slightly convex upwards, up to approximately 25-30% volatilization, while the remaining portion of the curves are slightly convave upwards, indicating that a zip reaction is taking place from the polymer chain ends.

D. Production of Volatiles during Degradation:

Madorsky[86] studied the bulk thermal degradation of poly-M-methyl styrene in vacuum at 350°C. He found the volatile products consisted of 44.4% M-methyl styrene monomer and 7.3% xylene. Simha[87] reported a value of 42% P-methyl styrene monomer yield during the bulk thermal degradation of poly-P-methyl styrene.

In the present work the bulk thermal degradation of methyl ring-substituted styrene polymers studied in vacuum at 330°C, produced monomeric products volatile at room temperature. The volatile products detected by V.P.C. ~~and Pyc-argon~~ were the corresponding monomer for all polymers and small quantities of xylene, trimethyl benzene and tri & tetramethyl benzene for the mono-, di-,

Table 20 (a)

Thermal Degradation of PMS_1 Polymer at 330°C.

Initial M.Wt. 138,000

Time of heating (mins.)	Extent of Volat. %	M.Wt. x 10^{-3}	%Volat at R.T.	Non-monomer/ Monomer	n x 10^3	Solubility %
1	2.7	89	-	-	0.44	-
2	4.5	77	-	-	0.61	-
5	6.8	80	-	-	0.52	94.0
20	8.2	47	-	-	1.45	-
15	8.5	42	-	-	1.72	-
33	10.4	43	-	-	1.60	-
29	12.2	37	-	-	1.95	-
45	14.7	-	45.6	1.20	-	-
47	15.5	-	44.9	1.23	-	-
142	32.6	-	44.1	1.27	-	-
145	33.7	16	42.9	1.33	4.04	-
243	46.3	13	-	-	4.45	-
245	48.3	-	43.5	1.30	-	-
270	58.7	-	44.4	1.25	-	-
384	77.9	-	45.6	1.20	-	7.0

PMS = P-methyl styrene.

Table 20 (b)

Thermal Degradation of PMS_2 Polymer at 330°C.

Initial M.Wt. 245,000

Time of heating (mins.)	Extent of Volat. %	M. Wt. x 10^{-3}	% Volat. at R.T.	Non-monomer/ monomer	n x 10^3
5	4.4	95	-	-	0.71
7	4.7	64	-	-	1.28
3	6.5	101	-	-	0.61
75*	8.1	77.5	-	-	0.92
67*	8.4	66	-	-	1.16
36	8.8	59	-	-	1.34
60	12.5	52	-	-	1.51
90	14.5	44	-	-	1.81
60	14.8	54	-	-	1.38
78	18.6	36	-	-	2.19
130	23	40	43.8	1.28	1.79
168	32.5	18	-	-	3.95
166	37.7	20	-	-	3.20

* These experiments were carried out at 320°C.

Table 20 (c)

Thermal Degradation of PMS_3 Polymer at 320°C.

Initial M.Wt. 420,000

Time of heating (mins.)	Extent of Volat. %	M.Wt. x 10^{-3}	$\alpha \times 10^3$
60*	10.7	50.5	1.81
50	19.5	26	3.38
150	50.1	23	2.28

* This experiment was carried out at 320°C.

Table 21

Thermal Degradation of MMS Polymer at 330°C.

Initial M.Wt. 246,000.

Time of heating (mins.)	Extent of Volat. %	M.Wt. x 10^{-3}	%Volat. at R.T.	Non-monomer/ Monomer	n x 10^3	Solubility %
1	3.1	150	-	-	0.28	97.4
5	3.2	91	-	-	0.78	-
15	7.7	70	-	-	1.08	-
45	11.3	69	-	-	1.04	90.1
60	14.4	50.5	-	-	1.52	-
85	19.3	40	-	-	1.90	-
130	28.3	19.5	-	-	3.86	-
160	29.2	23.5	-	-	3.08	-
180	41.4	11.5	46.3	1.16	5.54	-
268	45.3	-	44.6	1.24	-	-
-	58.8	-	43.8	1.28	-	-
487	66.7	9	-	-	4.21	10.0
-	73.8	-	44.8	1.23	-	-

MMS = M-methyl styrene.

Table 22

Thermal Degradation of OMS Polymer at 330°C.

Initial M.Wt. 160,000

Time of Heating (mins.)	Extent of Volat. %	M. Wt. x 10^{-3}	% Volat. at R.T.	Non-monomer/ Monomer	n x 10^{3}
2	4.1	67	-	-	0.95
3	9.9	36	-	-	2.22
3	10.7	37	-	-	2.12
8	16.5	25	-	-	3.21
22	25.1	20	47.8	1.09	3.69
30	34.1	14	47.9	1.09	4.83
40	37.2	13	49.0	1.04	4.97
-	37.5	-	48.0	1.08	-
51	43.4	13	-	-	4.50
80	61.8	7	-	-	5.72
190	76.9	7	-	-	3.16

OMS = O-methyl styrene.

Table 27

Thermal Degradation of 2,5-Di.MS ... at 210°C.

Initial Wt. ... gms.

Time of heating (mins.)	Extent of Volat. %	k_1 Vol. x 10^{-3}	% Volat. as K.T.	Non-monomer/ Monomer	n x 10^{3}
1	1.7	83	-	-	0.99
2	3.1	48	-	-	2.17
3	7.4	56	-	-	1.62
4	7.7	37	-	-	2.72
6	9.8	32	-	-	3.16
11	14.2	21	-	-	4.83
17	27.0	13	52.8	0.894	6.85
35	32.7	12	-	-	6.84
24	38.4	10	-	-	7.57
50	40.8	10	-	-	7.25
-	48.8	-	53.0	0.887	-
120	64.4	5	-	-	8.84
150	68.9	7	-	-	5.30
182	77.8	5	53.6	0.866	5.29

2,5/Di.MS = 2,5-dimethyl styrene.

Figure 34 (a)

Change Of Molecular Weight With Extent Of Volatilization

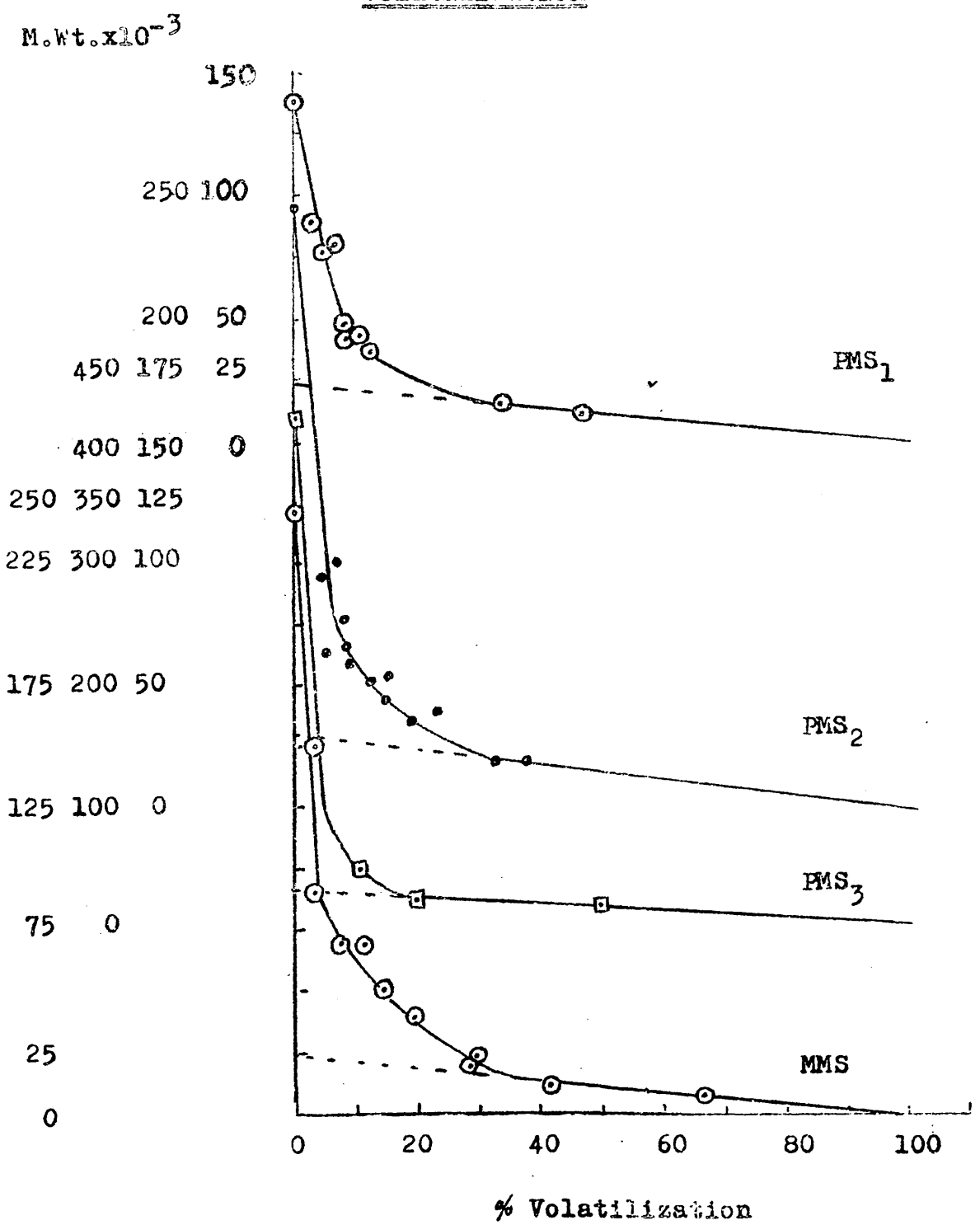
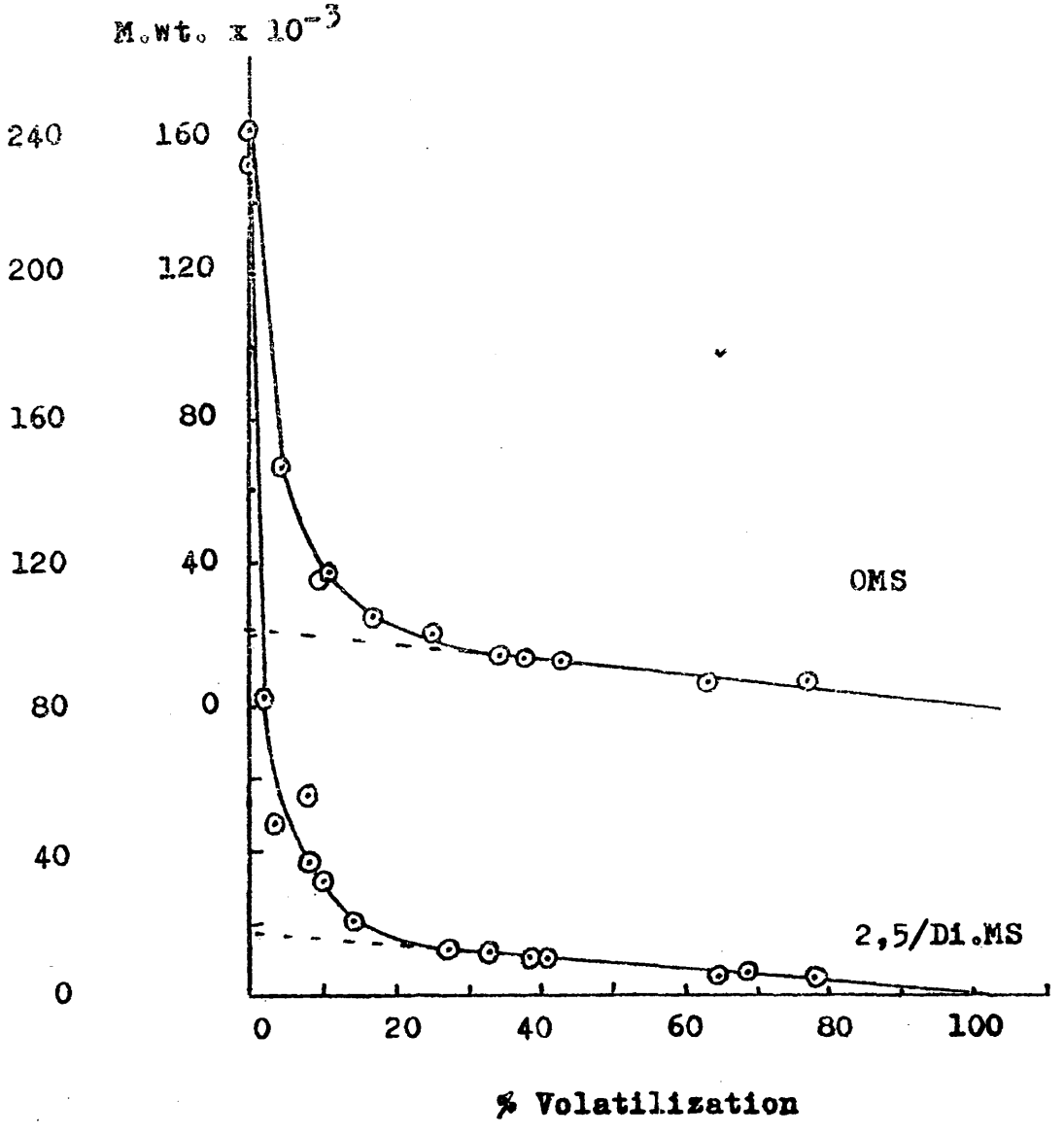
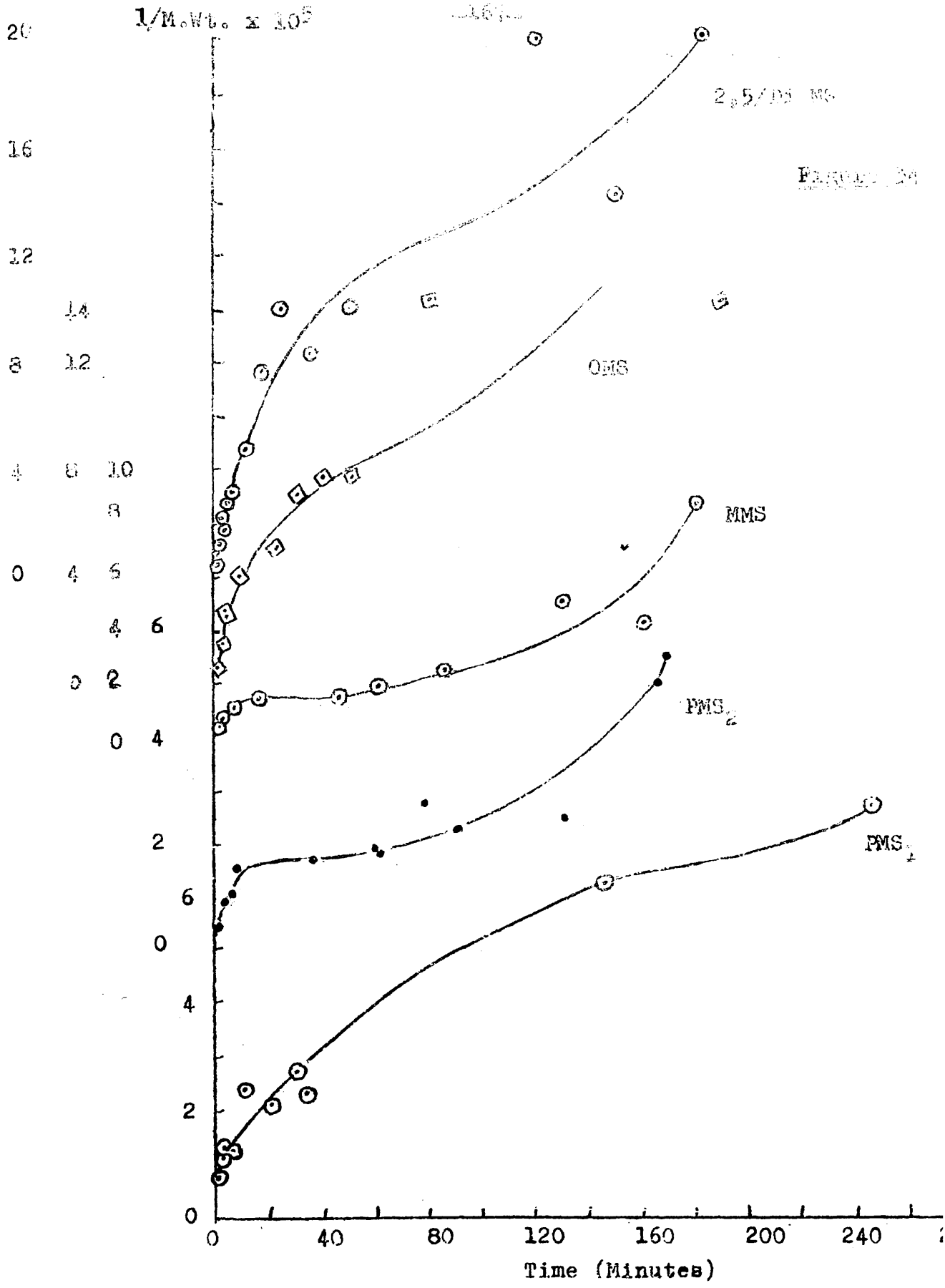


Figure 33 (b)

Change Of Molecular Weight With Percent Of Volatilization




1/M.Wt. x 10⁵
20
16
12
8
4
0
14
12
10
8
6
4
2
0
6
4
2
0
2,5/05 MS
OMS
MMS
PMS₂
PMS₁
0
40
80
120
160
200
240
Time (Minutes)

and trimethyl styrene polymers respectively.

The non-monomeric volatile products i.e. fragments larger than monomer, such as dimer, trimer.....etc, (volatile at the degradation temperature - involatile at room temperature) and appear as a wax like deposits on the sides and lid of the molecular still, were not identified.

The yields of products volatile at room temperature, together with the ratios of non-monomer to monomer, at various stages of the degradation reaction are also quoted in Tables 20-24. It can be observed that these ratios remain sensibly constant throughout the course of the reaction at the given temperature.

The experimental results indicate that there is a small tendency for the products volatile at room temperature, principally monomer to increase in the following order:-

$$2,5\text{-Di.MS} > \text{OMS} > \text{MMS} > \text{PMS}$$

It was assumed that the phenyl groups stabilize the styrene radical to such an extent that a good yield of monomer is obtained, although reactive hydrogen atoms for transfer are present. Thus it can be presumed that the introduction of methyl groups in the styrene benzene ring increases the stability of the radicals produced, which in turn results in an increase in the monomer yield.

Moreover, it was pointed out before that monomer is produced in a radical unzipping process, initiated at the chain ends, while non-monomeric volatile products are formed by intramolecular transfer process from the same long chain radicals. Therefore, there could be a small decrease in the probability of transfer through the -α- hydrogen atoms in the case of the methyl styrene polymers studied.

E. Rate of Production of Volatiles during Degradation:

Fig. 35 illustrates the change in relative rates during degradation with extent of volatilization. Also the plots of extent of volatilization as a function of time of degradation are shown in Fig. 36.

Fig. 36 indicates that there is no inhibition period in the initial stages of the reaction, although the slight curvature in the lines obtained confirms that the rate of production of volatile material increases early in the reaction.

The data quoted in Tables 20-23 shows, roughly, that the volatilization reaction proceeds at a faster rate in the case of OMS and 2,5-Di.MS polymers than PMS and MMS polymers, which indicates their lower thermal stability.

Fig. 35 shows that the rate of production of volatile material reaches a maximum in the range of about

Table 24

Percentage Monomer Produced.

Polymer	Monomer	%
P-methyl styrene.	P-methyl styrene.	42
M- " "	M- " "	43
O- " "	O- " "	46

13-15% volatilization at 330°C for all polymers studied and 15-17% volatilization at 350°C for P- and M-methyl styrene polymers. Madorsky found a maximum rate at about 23% volatilization for MMS polymer degraded at 350°C.

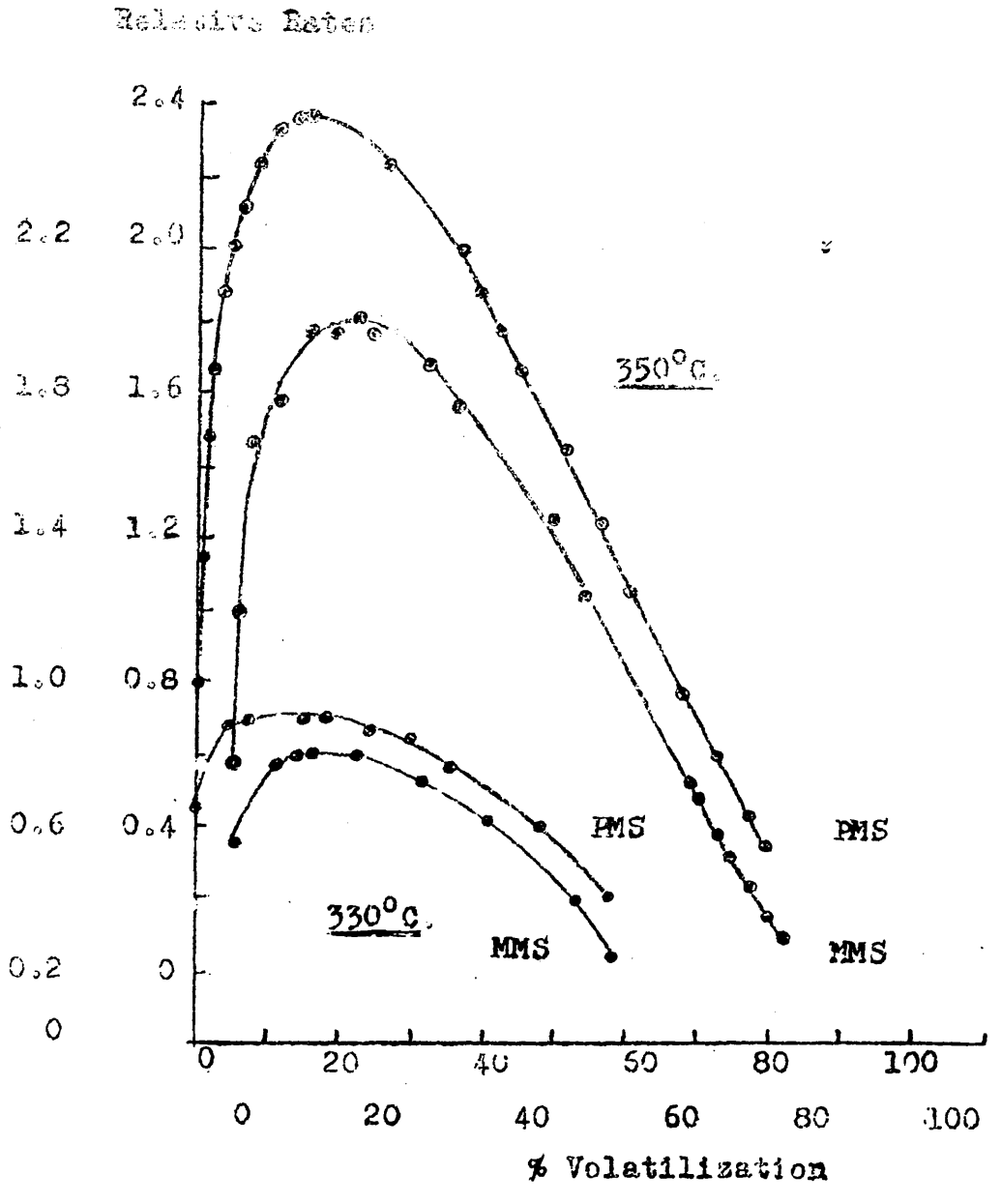
The occurence of a rate maximum in the bulk thermal degradation of polystyrene is discussed in Chapter 4. It has been shown that its chain scission phase of the reaction is just complete at approximately 30% volatilization. It exhibits a maximum rate at about 35-40% and 25-30% volatilization at 350° and 330°C respectively, compared with 15-17% and 13-15% volatilization at the corresponding temperatures, for the methyl ring substituted styrene polymers, where the chain scission phase is complete at approximately 25-30% volatilization.

According to Simha and Wall's theoretical expression, Fig. 35 indicates that the kinetic chain length of the reaction is long, since the plots are not straight lines but curved. On the other hand, Fig. 33 indicates that the kinetic chain length is shorter than for polystyrene.

Therefore, it can be concluded that the decrease in the kinetic chain length and the increase in the rate of chain scissions could account for the occurence of the rate maxima at lower conversions compared with polystyrene.

Figure 35 (a)

Change Of Reactive Areas With Extent Of Volatilization.



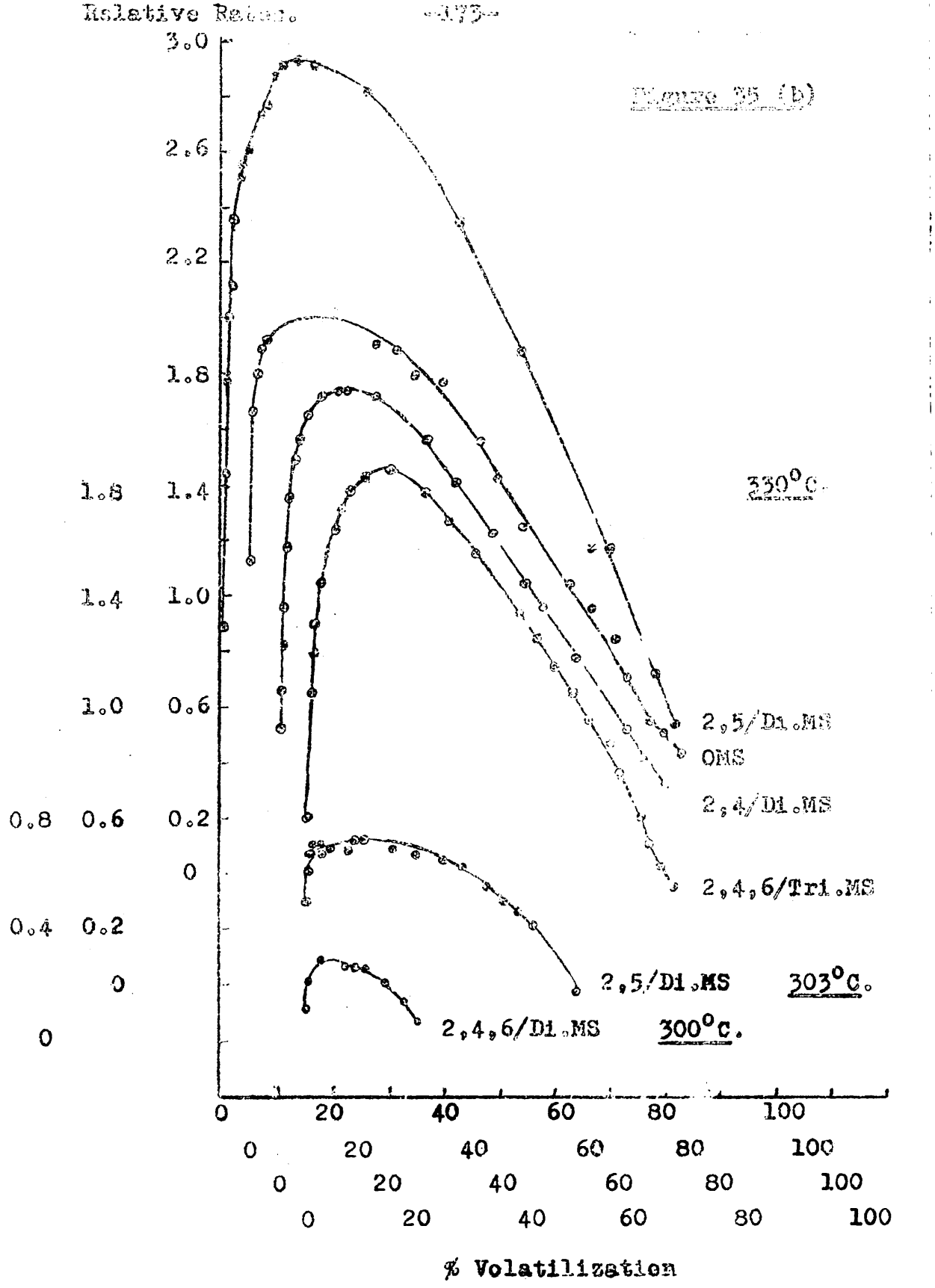

Relative Return.
Figure 35 (b)
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
0
330°C.
2,5/Di.MS
OMS
2,4/Di.MS
2,4,6/Tri.MS
2,5/Di.MS 303°C.
2,4,6/Di.MS 300°C.
0 20 40 60 80 100
% Volatilization

Figure 36 (a)

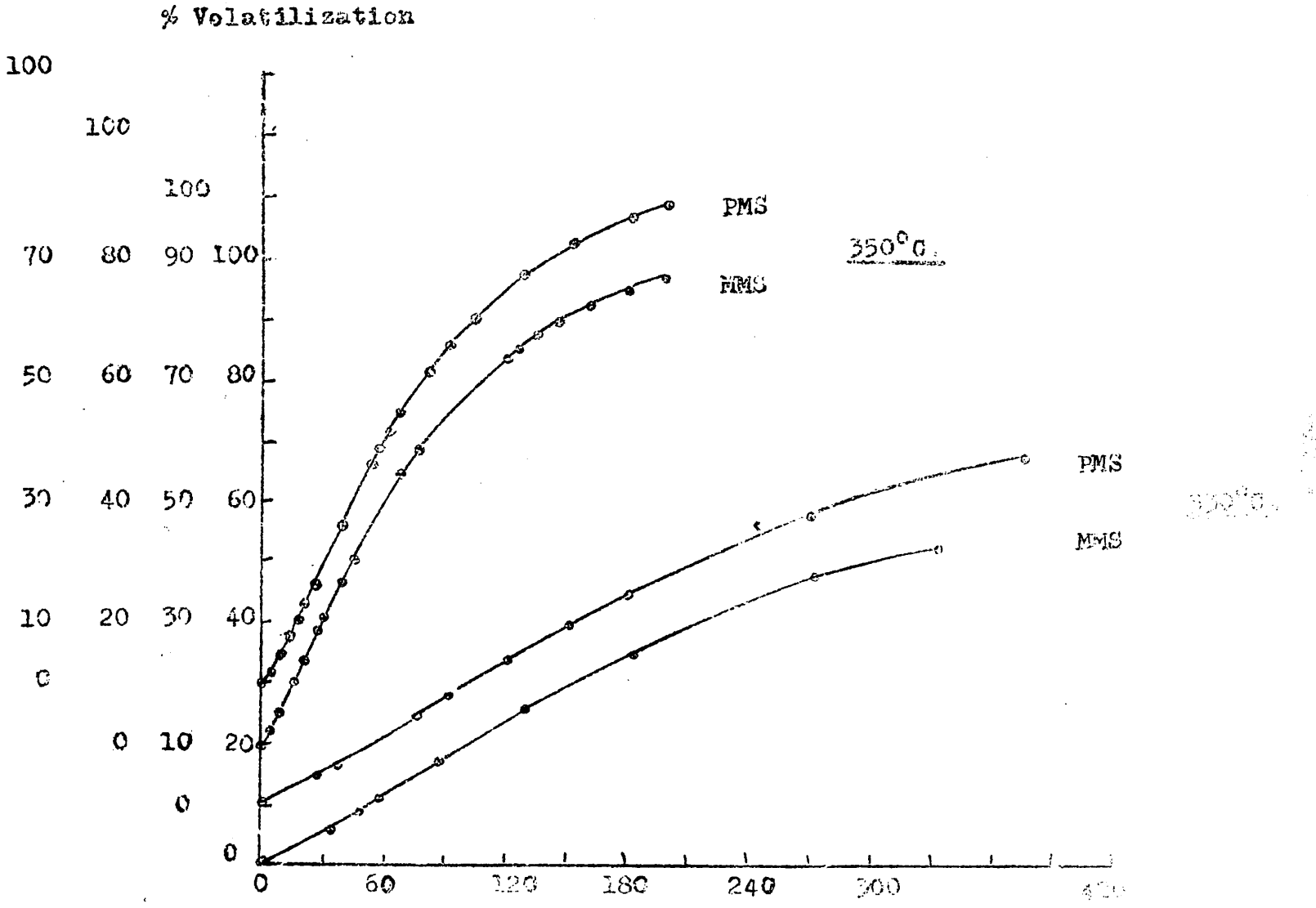
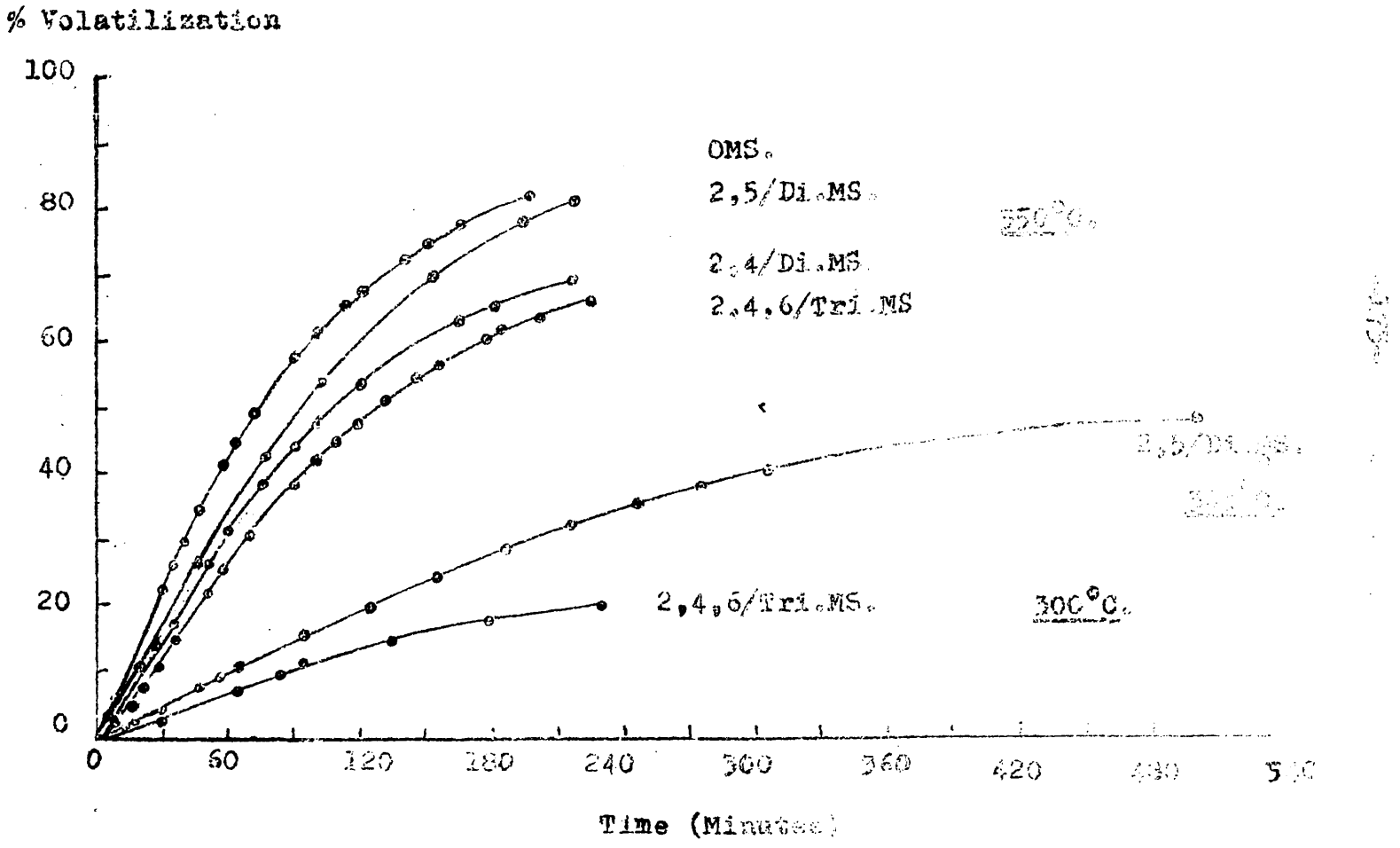

% Volatilization
100
100
100
70 80 90 100
50 60 70 80
30 40 50 60
10 20 30 40
0
0 10 20
0
0
PMS
MMS
350°C.
PMS
MMS
0
60
120
180
240
300

Figure 36 (b)


% Volatilization
100
80
60
40
20
0
0
60
120
180
240
300
360
420
480
OMS.
2,5/Di.MS.
2,4/Di.MS.
2,4,6/Tri.MS
350°C.
2,4,6/Tri.MS.
300°C.
Time (Minutes)

F. Estimation of the Number of Bonds Broken:

The concentration of weak links, S, originally present in the methyl styrene polymers under investigation was estimated by applying the relationship:-

$$S = M_o/M_d - 1$$

Moreover, the number of bonds broken, N, per polymer chain at time t, was determined by using the following expression:-

$$N = Cl_o(1-x)/Cl_t - 1$$

Both methods were discussed in Chapter 4.

Fig. 37 illustrates the plots of the number of bonds broken per monomer unit as a function of extent of volatilization. The experimental results are summarized in Tables 20-23.and 25.

Beyond about 30% volatilization the values of the molecular weights of PMS and MMS polymers are not so reliable, since the residual polymer becomes partially insoluble. Some values indicating extent of solubility are quoted in Tables 20 and 21.

G. Determination of the Activation Energies:

The same technique as was applied in Chapter 4 for the determination of the activation energies, was used here. The data obtained are illustrated in Fig. 38 and summarized in Table 26.

Madorsky reported an activation energy of 56 k.

Figure 37 (a)

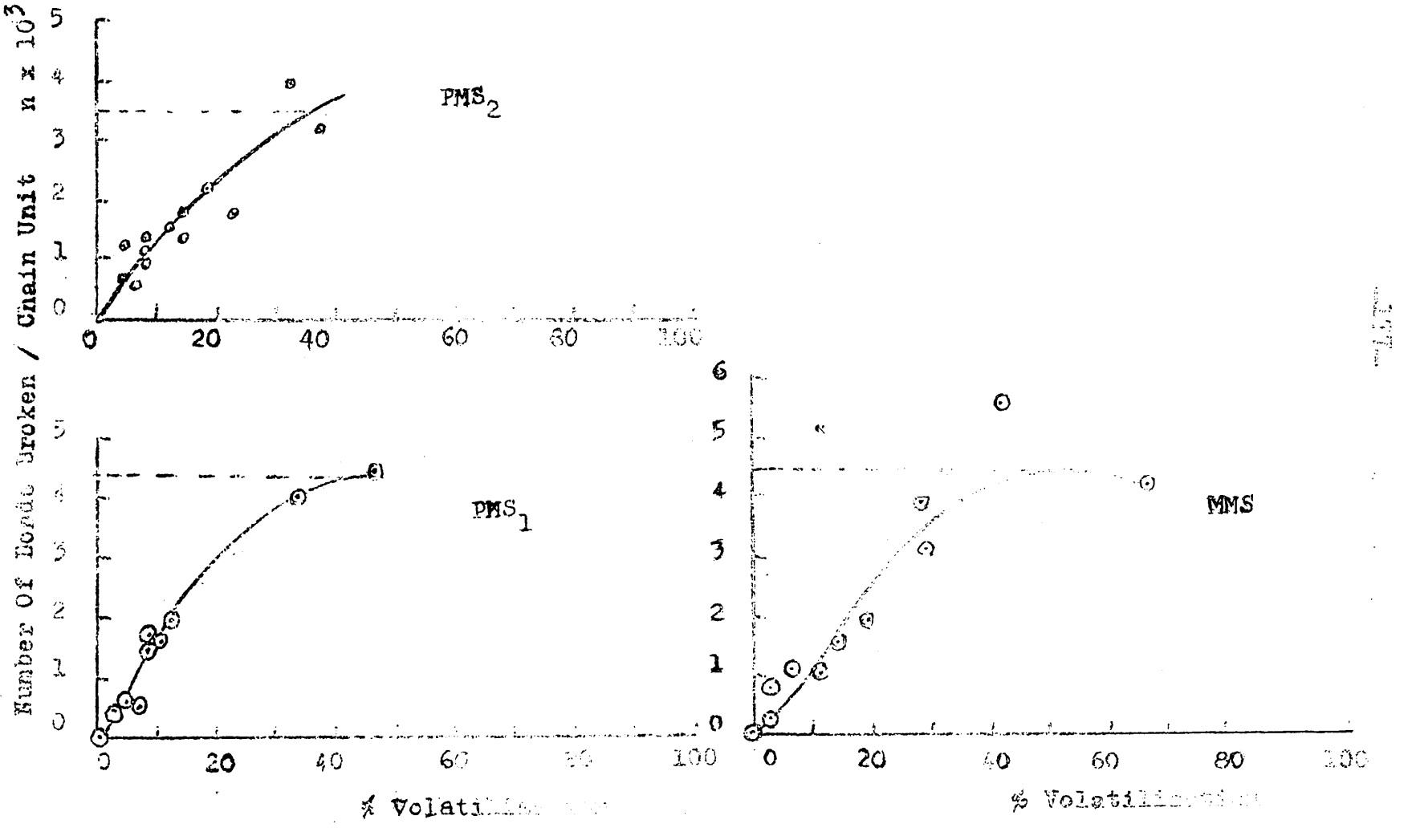

Number Of Bonds Broken / Chain Unit n x 10^3
PMS2
PMS1
MMS
% Volatilisation
% Volatilisation

Figure 37 (b)

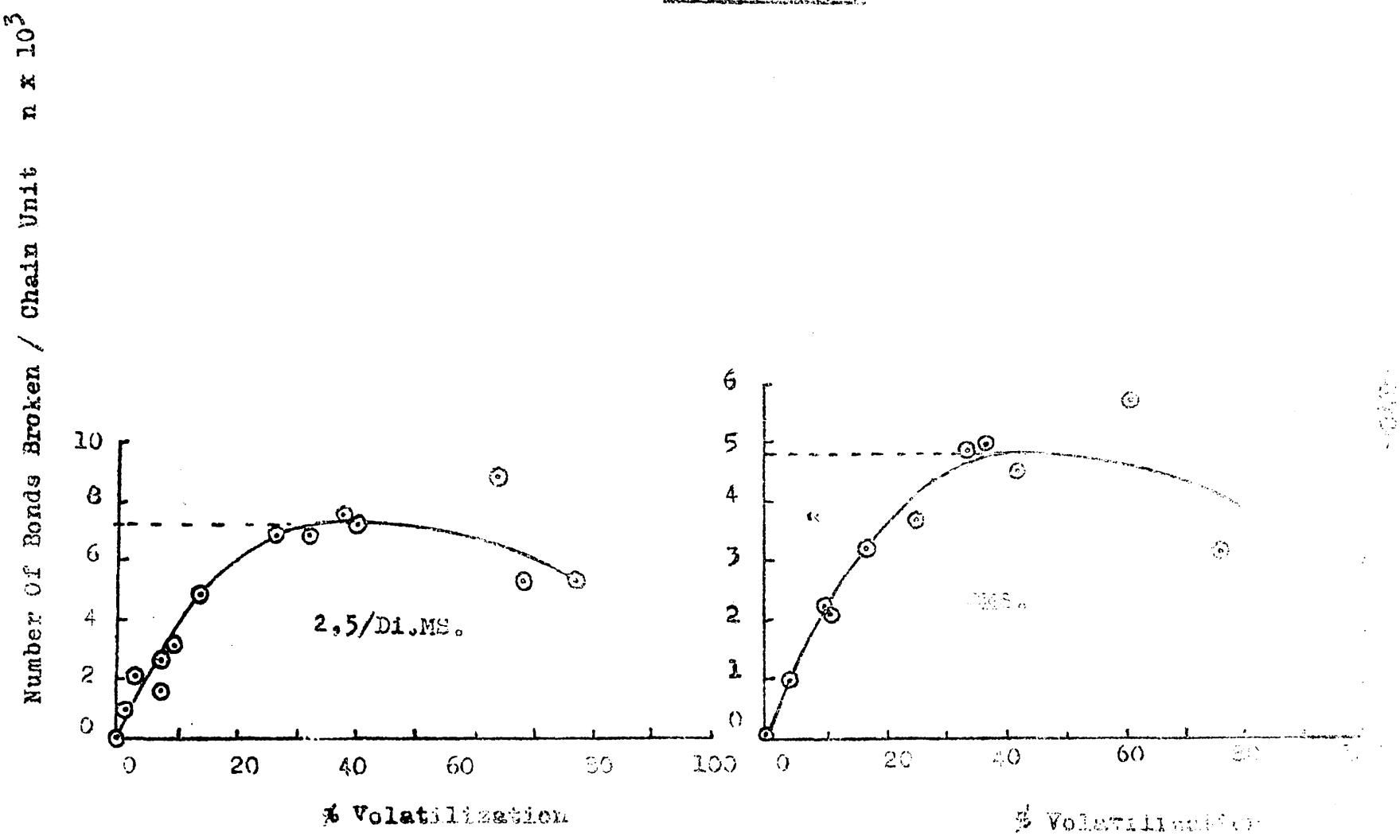

Number Of Bonds Broken / Chain Unit n x 10^3
10
8
6
4
2
0
0
20
40
60
80
100
2,5/Di.MS.
% Volatilization
6
5
4
3
2
1
0
0
20
40
60
% Volatilization

Table 25

Data of Weak Link Concentration for Polymethyl styrenes.

Polymer	Mode of Prepn.	Temp. of Degr. °C	M_o $\times 10^{-3}$	M_d $\times 10^{-3}$	n^a $\times 10^3$	n^b $\times 10^3$
PMS_1	Free R.	330	138	24	4.1	4.3
PMS_2	"	"	245	30	3.5	3.5
PMS_3	"	"	420	31	3.5	-
MMS	"	"	246	24	4.4	4.4
OMS	"	"	160	21	4.9	4.8
2,5/Di.MS	"	"	231	17	7.2	7.2

a Data obtained by extrapolation of molecular weight/extent of volatilization curves.

b Data obtained by extrapolation of number of bonds broken per chain unit/extent of volatilization.

cal/ mole for the thermal degradation of poly-N-methyl styrene.

The energies of activation measured in the region beyond 25-30% volatilization is assumed to correspond to the depolymerization reaction only. In the initial stages of the reaction the weak links present are breaking down and consequently the number of degradable molecules continuously increases.

The data in Table 26 shows that there is a reduction in the values of the activation energies, compared with those obtained for polystyrene (see Table 19 Chapter 4). Also there is a decrease in the values on passing from the mono- to the trisubstituted polymers.

H. Discussion and Conclusion:

In comparing the bulk thermal degradation behaviour of the methyl ring-substituted styrene polymers with polystyrene, it is clear that the introduction of methyl groups does not alter the main features of the degradation reaction.

The molecular weight falls rapidly in the initial stages of the reaction, followed by a gradual decrease. Volatile products are formed throughout the course of the reaction. Also rate maxima occur which, although earlier in the reaction, compared with polystyrene, could also be attributed to a decrease in the rate of production

Figure 38 (a)

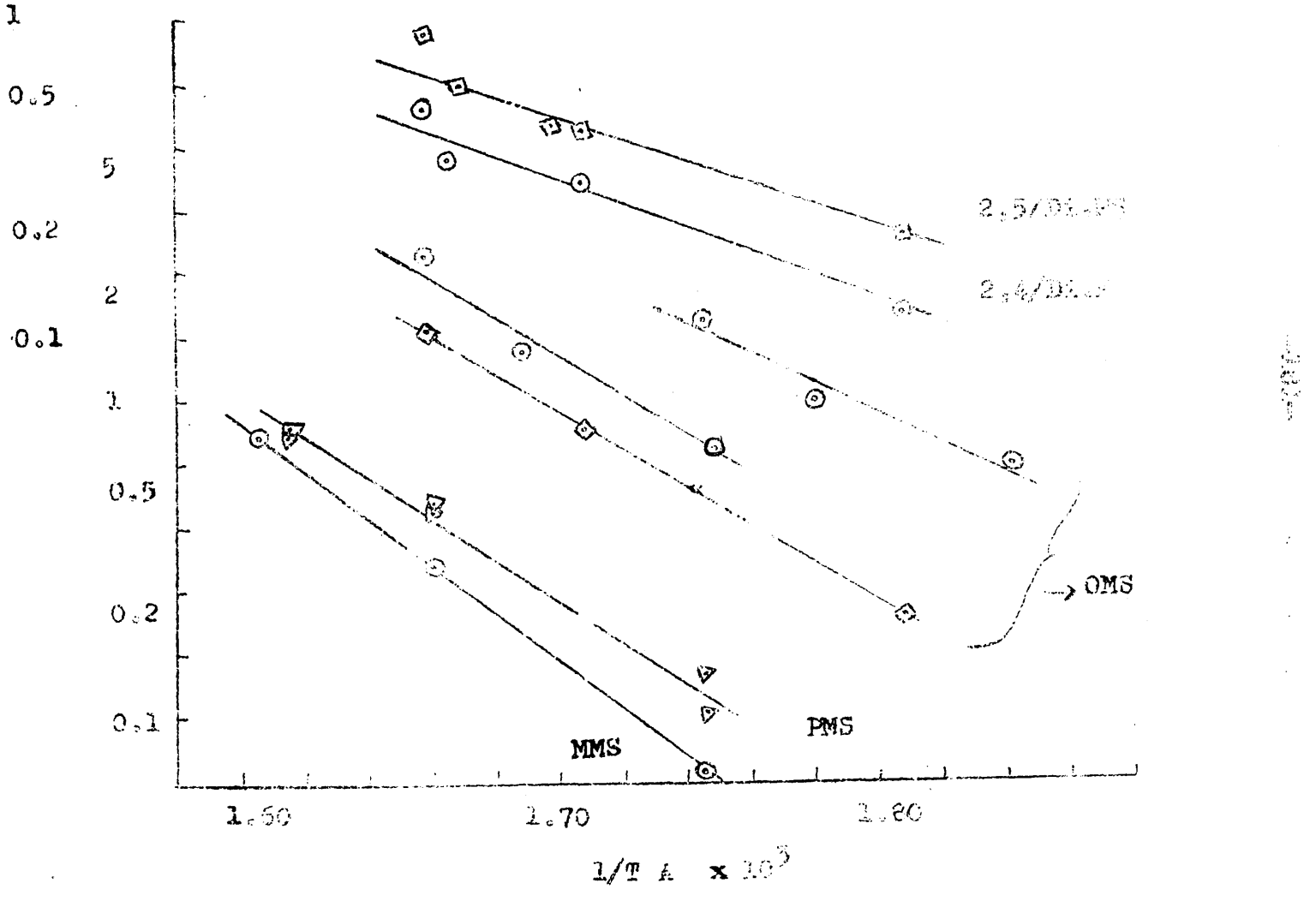

Relative Rates
1
0.5
0.2
0.1
5
2
1
0.5
0.2
0.1
OMS
PMS
MMS
1.60
1.70
1.80
1/T A x 10^3

Figure 38 (c)

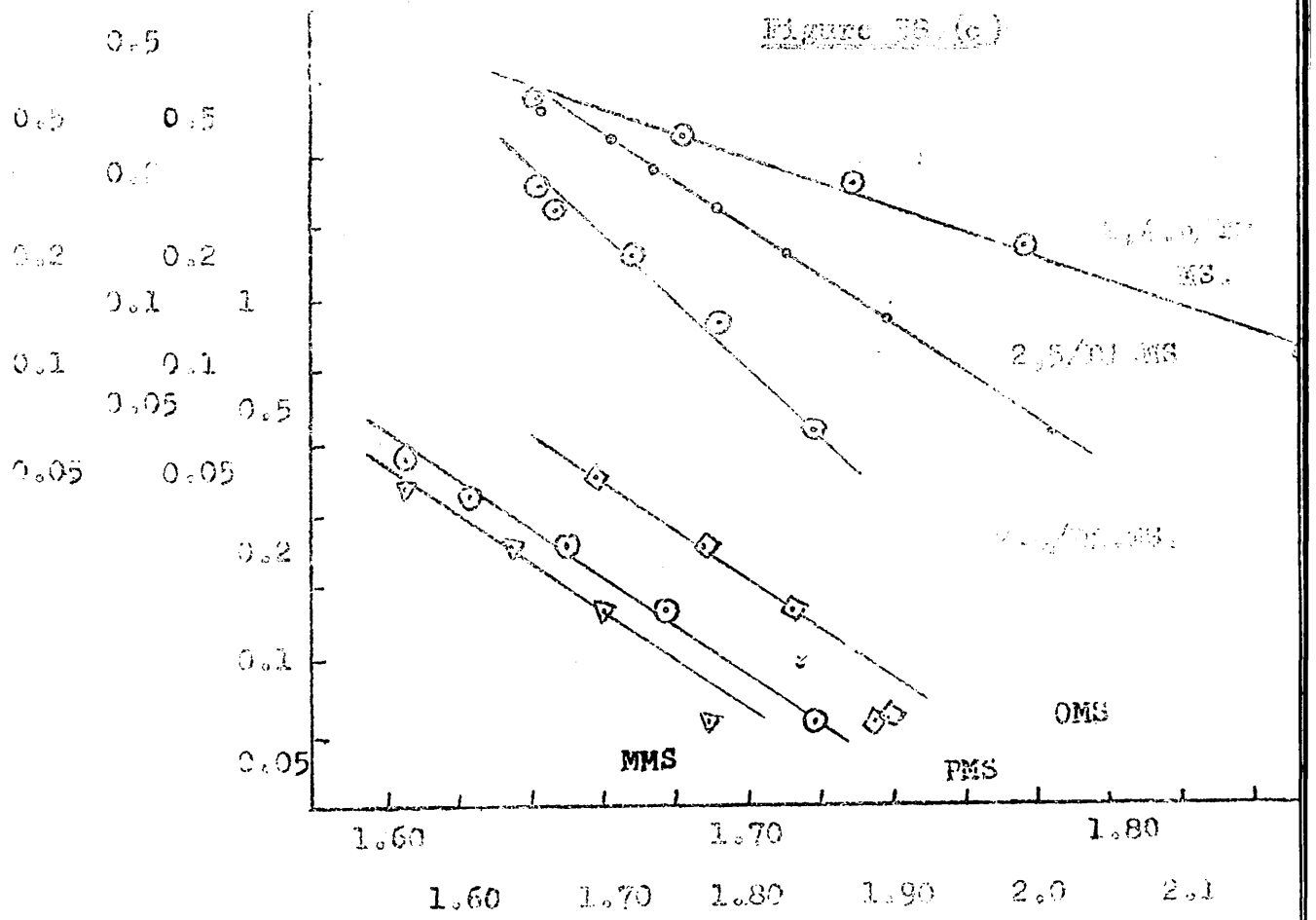


Figure 38 (d)

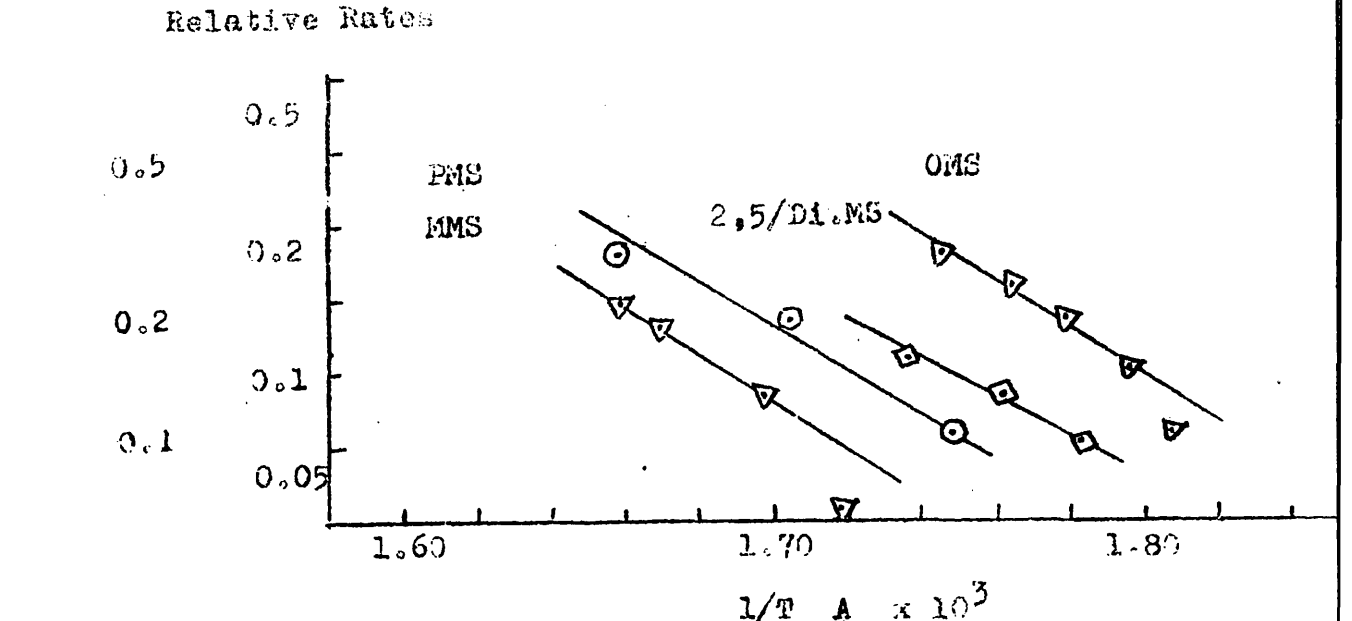


Table 26

Activation Energies.

Polymer	Temp. range °C	Extent of Volat. %	Activation energy k.cal/mole.
PMS	300-350	Initial (a)	33.7
"	330-299	57.2 (b)	27.8
"	350-309	79.2 (c)	31.2
MMS	300-350	Initial	34.6
"	330-309	52%6	29.3
"	350-319	76.9	30.9
OMS	280-330	Initial	27.5
"	299-330	"	27.9
"	270-300	"	21.7
"	300-280	41.4	29.3
"	330-302	86.3	31.0
2,4/Di.MS	280-330	Initial	17.1
"	330-269	69.9	17.6
2,5/Di.MS	280-330	Initial	15.3
"	303-282	48.8	24.3
"	330-224	81.6	12.4
2,4,6/Tri.MS	330-184	66.3	6.4

(a) = Figure 38 (a)

(b) = " " (b)

(c) = " " (c)

of volatile material or an increase in the rate of chain scissions. This is in accordance with the fact that these polymers have a shorter kinetic chain length than polystyrene. Moreover, the activation energy of the reaction is reduced, thus accounting for their lower thermal stability.

The experimental results quoted in Table 25 show that the methyl polymers have a higher weak link concentration, compared with polystyrene (see Table 19), and that the order of abundance of weak links could be written as:-

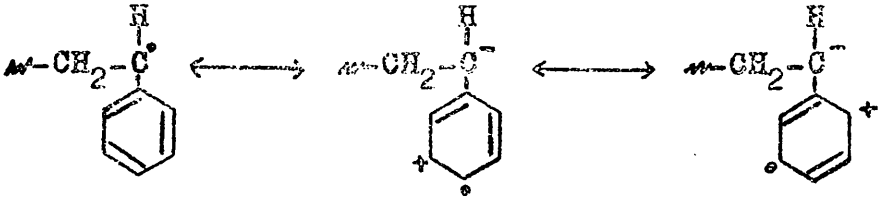
$$2,5\text{-Di.MS} > \text{OMS} > \text{MMS} \simeq \text{PMS}$$

It may be concluded that the concentration of weak links present in a polymer chain depends on the number and position of the methyl group in the benzene ring.

It was mentioned earlier in Chapter 3 that Imoto et al[65] reported that in the radical polymerization of some P-substituted styrenes; styrenes with more electron-attracting substituents show a greater overall rate of polymerization. They assumed that ionic structures are important in radical polymerization.

Ayrey, Levitt and Mazza[88] suggested that polar effects are important in polymer radical-radical interactions, especially in mutual termination reactions of the free radical polymerization of some P-substituted styrenes.

They assumed that the polystyrene radical, by virtue of the phenyl group is essentially an electronegative radical.



and that this effect is considerably increased by the P-methoxy group, since it is an effective electron donating group.

Moreover, applications of Hammett's equation to radical copolymerizations of styrene and substituted styrenes[89] were earlier indications of polar effects in free radical reactions.

Recently, it was[88] pointed out that , although free radicals are neutral species, yet changes in structure may invoke slightly nucleophilic or electrophilic character.

Grassie and Cameron, as stated previously, suggested the possibility of occasional polymerization of styrene radical through a canonical form of the growing polymer radical, at the ortho and para positions, since the polystyryl radical is stabilized by conjugation.

In the present work, the experimental results in Chapters 3 and 5 show that methyl substitution in

the benzene ring results in an overall reduction in the rate of polymerization and an increase in the number of weak links compared with styrene. The former may be attributed to an increase in the resonance stability by hyperconjugation and consequently a decrease in the reactivity of the free radicals. The latter could be explained in terms of an increased probability of the "abnormal" polymerization, either by hyperconjugative resonance[89,90] or by increasing the electron density in the benzene ring. Since methyl groups are electron releasing, O-,P- directing , ~~although it had been reported earlier to be M-directing~~ this , ~~therefore~~, will cause the activation of these sites for polymerization.

CHAPTER 6

REVIEW OF THE PROBLEM AND SUGGESTIONS FOR FUTURE WORK

In this Chapter, it is intended to give a general picture of the experimental results obtained and to outline further possible courses of investigation.

The studies of the bulk thermal degradation of "living" polymers have clearly shown that these polymers also contain thermo-labile structures similar to those in samples prepared by free radical means. This evidence supports the view that weak links are the same in both types of polymers. However, what seems rather surprising is the similarity of weak link concentration in living and free radical polymers. Because of the different modes of preparation of these polymers, it is to be expected that at the very least the concentration of weak links would be different.

The bulk thermal degradation of methyl ring-substituted styrene polymers shows that these polymers also contain thermo-labile structures in a higher concentration than polystyrene, and that these break down more readily than those in polystyrene. This suggests that methyl substitution in the styrene ring has a profound influence in increasing the number of

thermo-labile structures in the polymer chain. Though it might have been expected that blockage of the ortho and para positions by methyl substitution may prevent or at least hinder the occurence of abnormalities caused by reaction of the polystyryl radical in its canonical forms, yet the experimental results suggest the probability that methyl groups may activate the benzene ring for abnormal polymerization.

Moreover, it was found that during the thermal degradation of PMS and MMS polymers, the residual polymer became partially insoluble, and that insolubility increased with extent of volatilization. This could be due to cross-linking. No further studies were made at this point.

From the polymerization studies of methyl styrene monomers, it could be concluded that methyl substitution renders the radicals more stable and thus less reactive towards free radical polymerization, compared with styrene.

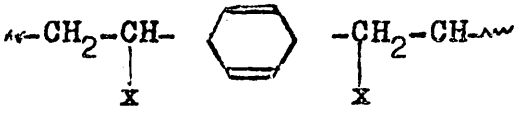
Therefore, on the immediate problem of weak links, it has to be admitted that inspite of the existing information, their exact structure or mode of formation is still not known with certainty.

A further systematic investigation of substituted styrenes may be useful in clarifing this problem, since

it is obvious from the present work that methyl substitution in the benzene ring increases the concentration of thermo-labile structures. Therefore, it would be of interest to examine the effect of other substituents, such as the nitro group, which is known as electron attracting and also the methoxy group, as might be expected to have different concentrations of weak links from these polymers already studied, with the methyl group as electron releasing.

Also, a systematic study of ring-substituted styrene polymers (including methyl substitution) prepared by ionic methods, appears to be a course worth examining.

It is known that benzene can copolymerize with vinyl acetate[92] to give structures of the type:-



Since it has been suggested that weak links are quinonoid structures[31], then it is interesting to speculate how far the above structures would behave like the weak links in polystyrenes. Therefore, a study of such co-polymer appears worth while.

Finally, the results of the present work can be briefly summarized as follows:-

1. The thermal degradation of "living" polystyrenes exhibits the same features observed for free radical

prepared polymers.

2.The concentration of thermo-labile structures is of the same order of magnitude.

3.The thermal degradation of methyl ring-substituted styrene polymers, show also, the main features observed for polystyrenes.

4.The concentration of thermo-labile structures is higher than in polystyrenes.

5.The polymerization studies of methyl styrene monomers show that there is a reduction in the overall rate of the thermally catalyzed polymerization, compared with styrene.

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